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NONFERROUS SMELTING AND REFINING

1949

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TRANSACTIONS

OF THE

AMERICAN INSTITUTE OF MINING AND METALLURGICAL ENGINEERS

(INCORPORATED)

Volume 182

*American Institute of Mining,
Metallurgical, and Petroleum Engineers*

EXTRACTIVE

METALLURGY DIVISION

1949

TECHNICAL PAPERS AND DISCUSSIONS PRESENTED BEFORE THE DIVISION AT
MEETINGS HELD AT NEW YORK, FEBRUARY 1944, CHICAGO, FEBRUARY
1946, NEW YORK, MARCH 1947 AND FEBRUARY, 1948.

PUBLISHED BY THE INSTITUTE
AT THE OFFICE OF THE SECRETARY

29 WEST 39TH STREET
NEW YORK 18, N.Y.

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AMERICAN INSTITUTE OF MINING AND METALLURGICAL ENGINEERS
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PRINTED IN THE UNITED STATES OF AMERICA

THE MAPLE PRESS COMPANY, YORK, PA.

5-13-30
min. 200
of Mining
Engineering
10933-2163
Vol 7300

FOREWORD

THE last volume of TRANSACTIONS in the field of extractive metallurgy was No. 159 (1944), Reduction and Refining of Nonferrous Metals. It totaled 555 pages and contained for the first time in AIME literature a substantial presentation of aluminum and magnesium extractive processes.

Late in 1948 a new Extractive Metallurgy Division of the Institute was formed. The nucleus was the former Technical Committees on the Reduction and Refining of Copper, Lead and Zinc, and Aluminum and Magnesium. The new Division, however, has spread far beyond the scope of these three and now has technical committees on Aluminum and Magnesium, Copper and Nickel, Lead and Zinc, and Titanium; and commodity committees including Electrolytic Refining, Hydrometallurgy, Pyrometallurgy, and Economics and Statistics. Other committees both on commodity and functional lines will be formed.

The present volume, however, does not include papers published since the formation of the new Division. It contains papers on three alumina processes that were studied during the war. One describes the bauxite combination process which was employed on a commercial scale which still continues, and the other two describe the results of semicommercial plants operating on clay. It is unfortunate that the latter two plants, built and operated with Government funds, were not run long enough to obtain additional engineering data and to establish a better idea of operation costs.

We are fortunate in being able to present an excellent series on magnesium production. Dow's seawater plant at Velasco and Diamond Alkali's operations, in which the magnesium chloride are produced in conjunction with the Solvay soda process, are two commercial plants. The other three papers are on research or pilot-plant studies. The "fireless cooker" is a modification of the Pidgeon ferrosilicon process used commercially during the war.

Two papers are on vacuum-process preparation of lithium which is along the basic lines used in the Pidgeon magnesium process.

There are ten papers on copper, lead, and zinc and one paper each is devoted to manganese, mercury, vanadium, and unit processes.

The volume is fairly well balanced and the profession and industries are indebted to the Program and Division Chairmen who arranged the programs that comprised the papers making up this volume.

JOHN D. SULLIVAN, *Chairman*
Extractive Metallurgy Division

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The Combination Process for Alumina

BY JUNIUS D. EDWARDS*

WHEN Charles Martin Hall invented the electrolytic process for the production of aluminum, one basic requirement was a supply of pure alumina. Now, more than 50 years later, the same requirement still holds, and there are no technical straws in the wind to indicate that this situation is likely to change. Long ago, Aluminum Company of America took a number of steps to see that this country should not face shortages of alumina and aluminum in time of emergency. As one step to this end, the Company developed and used a supply of bauxite in South America in order to conserve dwindling Arkansas reserves. Another, and more a program than a step, was to investigate every type of process that might bear the possibility of utilizing the low-grade ores of aluminum that are more plentiful than bauxite. It is a long story, but the investigation included electric-furnace processes, acid extraction processes and alkaline extraction processes, with or without preliminary furnace and sinter treatments. Some of the processes developed were operated in commercial production. This work has been continuous since the first World War.

The turn of the wheel came sooner than was expected when, in 1942, bauxite shipments through the Caribbean became uncertain and hazardous through the operation of submarines. The tremendous requirements of aluminum for the war effort were consuming high-grade bauxite at an alarming rate and a national search

for substitutes began. High-grade bauxites, for technical and economic reasons, have been defined as those containing about 7 per cent or less of silica. While bauxite of this grade was limited in amount in the United States, there was in sight a substantially greater volume of low-grade, high-silica bauxite not amenable to economic treatment by the Bayer process, but richer in alumina than the clays or other available low-grade ores. It was at this point, and after several years of intensive research on this particular phase of the problem, that Aluminum Research Laboratories brought to completion the invention of one of its research staff, which made practical the utilization of large reserves of low-grade bauxite in America.

BAYER PROCESS

The Bayer process has been almost universally used for the production of alumina from bauxite. This process, in outline, comprises the digestion of finely ground bauxite in a solution of caustic soda (NaOH) under pressure and at an elevated temperature. Alumina in the bauxite goes into solution as sodium aluminate and the impurities—oxides of iron, titanium and silicon—remain undissolved. The undissolved residue, known as "red mud," from its color, is separated and run to waste. Aluminum hydrate ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) is precipitated from the solution of sodium aluminate, and the liquor containing the caustic soda and some alumina is returned to the process for digesting more bauxite. The aluminum hydrate, after washing, is calcined at a high temperature to produce

Manuscript received at the office of the Institute Nov. 29, 1944. Issued as TP 1833 in METALS TECHNOLOGY April 1945.

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alumina (Al_2O_3) for the electrolytic reduction process.

The red mud contains almost all of the impurities in the bauxite and also contains

pound of soda (calculated as sodium carbonate) are lost for each pound of silica in the red mud. This is the economic reason why 7 per cent silica has been con-

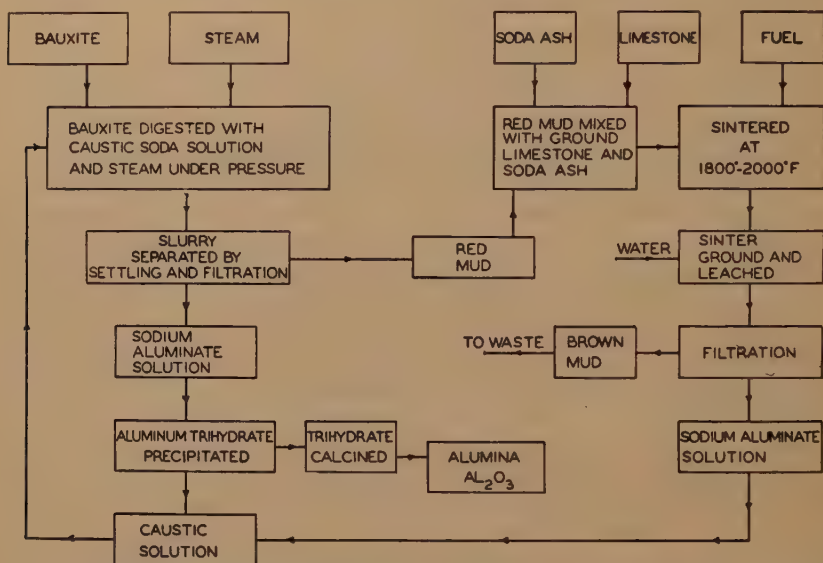


FIG. 1.—FLOWSHEET OF ALCOA COMBINATION PROCESS FOR PRODUCTION OF ALUMINA.



FIG. 2.—ONE OF A BATTERY OF SEVEN 250-FOOT KILNS AT EAST ST. LOUIS WORKS FOR SINTERING THE SLURRY OF RED MUD, SODA ASH AND LIMESTONE.

some alumina and some soda, since any reactive silica in the bauxite combines with both alumina and soda to form an insoluble sodium aluminum silicate. In this way, about one pound of alumina and one

considered a practical limit for bauxite that is to be classed as a high-grade ore. Low-grade bauxites high in silica can, of course, be treated by the Bayer process, but with increased loss of soda and alumina in the

red mud, reduced yields per ton of ore mined, and lower capacity for the plant. The new process largely eliminates this uneconomic loss of soda and alumina and makes practical the utilization of low-grade bauxites, of which there is a substantial supply available in the United States and elsewhere.

LIME-SODA PROCESS

Proposals have been made in the past to treat low-grade, high-silica ores by the lime-soda process. In this procedure, finely ground ore is mixed with limestone and soda ash. The mixture is then sintered to cause reaction of the lime with silica to form an *insoluble* calcium silicate, and reaction of the soda with alumina to form a *soluble* sodium aluminate. The sinter is leached with water or caustic soda solution to dissolve the soluble soda and alumina. This process is good in theory, but in practice the separation is not a sharp one; an undesirable amount of silica is solubilized and goes with the soda and alumina to the leach liquor, and more or less of the alumina remains insoluble. If, as originally proposed, the leach liquor is treated with carbon dioxide to precipitate the alumina, all the dissolved silica is also precipitated and the alumina usually contains about 2 per cent or more of silica, which makes it unsuitable for the production of pure aluminum. Various proposals have been tried to eliminate the silica from this solution, such as treating with steam in an autoclave. Only part of the silica is precipitated in this way, and the liquor thus treated usually retains sufficient of this impurity so that when the residual alumina is precipitated therefrom it contains about 0.3 to 0.8 per cent of silica. In another procedure, the alumina is precipitated by seeding and agitation and a low-silica product is obtained. Only a part of the alumina is recovered, however, and the silica is concentrated in the residual liquor. If the remaining alumina is then pre-

cipitated by carbonation to recover both soda and alumina, the silica is carried with it, and may amount to as much as 0.5 to 1.5 per cent. These various modifications



FIG. 3.—SCRUBBER COLLECTING DUST FROM KILNS.

of the lime-soda process have failed to produce commercially silica-free alumina from high-silica bauxite.

ALCOA COMBINATION PROCESS

A practical solution to the problem of economically utilizing high-silica bauxites has now been found. Ralph W. Brown, of the Chemical Development Division (East St. Louis) of Aluminum Research Laboratories, has invented a new process, which employs a sintering operation as a cyclic step in the Bayer process. In his process, the high-silica bauxite is given the customary Bayer alkaline digestion without regard to the considerable amounts of alumina and soda that are insolubilized by the silica and pass into the red mud. The red mud is not discarded, however, but after adjustment of its composition (by the addition of limestone and soda ash) is

put through a sintering operation. The sinter is then leached with caustic soda solution, which dissolves most of the alumina and soda but only a very small

to give the best results. There should be a slight excess of lime over that necessary for the formation of the insoluble dicalcium silicate ($2\text{CaO}\cdot\text{SiO}_2$), and there should also



FIG. 4.—BALL MILL IN WHICH SINTER IS GROUND AND SIMULTANEOUSLY LEACHED WITH WATER. RESULTANT SLURRY IS DISCHARGED THROUGH A SCREEN AND PUMPED TO THE FILTERS.

proportion of the silica. This leach liquor containing the alumina and soda is then returned to the digesters for the next cycle in the treatment of bauxite. The silica in the leach liquor, with an equal amount of alumina, again passes into the red mud; but most of the recovered alumina, together with that extracted from the bauxite, remains in the clear liquor and goes to the regular Bayer precipitation. By this cyclic procedure, an efficient process of producing alumina results, and the product is of standard Bayer quality, substantially free of silica, even though the sintering and leaching operations alone give an inefficient separation. An outline of the Alcoa Combination process is presented in the diagram of Fig. 1.

The composition of the red mud mixture to be sintered must be carefully adjusted

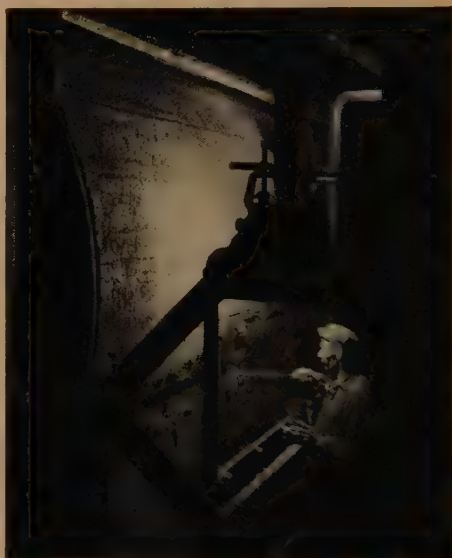


FIG. 5.—ROTARY FILTER FOR SLURRY FROM BALL MILL. BROWN MUD RESIDUE SHOWN ON FILTER SURFACE IS BEING SAMPLED BY OPERATOR.

be an excess of soda over the amount necessary to form sodium aluminate with the alumina present. There is some soda in the red mud, which has been carried over as the insoluble sodium aluminum silicate, and smaller amounts that have not been removed by washing. If lime was employed in the digester to causticize the sodium carbonate for the extraction of alumina, this lime will be present in the red mud and reduce the amount necessary to add for the sintering operation. It is practical, however, to adjust the additions of soda ash and limestone to the red mud sinter charge so that the caustic values in the leach liquor, together with the spent liquor from the precipitators, will supply all the caustic necessary for the digestion of the bauxite. This is possible because the sodium aluminate solution has a high caustic equivalent.

The red mud is intimately mixed with the necessary ground limestone and soda. The thick slurry, carrying about 60 per cent solids, passes to an agitator, which serves as a storage tank. From here it is fed at a uniform rate and sintered in a 250-ft. kiln, at a temperature of about 1800° to 2000°F. , to complete the reaction to form the insoluble silicate and the soluble aluminate. A porous, open sinter is desirable in order that leaching may be readily effected. In practice, the sinter as it leaves the kiln contains about 20 per cent alumina. The sinter discharge is a soft, friable product with a small proportion of harder lumps formed from local overheating. The sinter passes through a rotary cooler, after which it is screened and the oversize crushed.

The sinter is simultaneously ground and leached with water in a ball mill. The solution of caustic soda and sodium aluminate formed in this operation is separated by filtration. It is then pumped to the digesters, where it is mixed with bauxite and a new cycle of alumina extraction is started. The residue, after washing to remove soda and alumina values, is run to waste. The residue is called "brown mud," to distinguish it from the red mud of the Bayer process.

As previously noted, a small amount of silica is invariably dissolved during the leaching of the sinter. Also during the leaching, sodium ferrite or titanate, which may have been formed during the sintering, probably hydrolyze to liberate all or part of the soda they contain. For the

leaching solution, clear water or wash water from the various steps in the process may be used. The contained soda is thus returned to the process and utilized. It is desirable to maintain a concentration of caustic soda in the digesters sufficient to provide a ratio of alumina to soda in the liquor produced of about 0.8.

The hot mixture of sodium aluminate solution and red mud from the digesters is separated by settling and filtration. The clear aluminate solution goes to the precipitators, where by seeding, cooling and agitation, aluminum trihydrate ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) slowly forms. After filtration and washing, the hydrate is fed to kilns, where it is calcined to alumina (Al_2O_3), ready for the production of aluminum.

The Alcoa Combination process makes possible the economical extraction of about 85 to 90 per cent of the alumina in high-silica bauxites. This figure compares favorably with 80 to 85 per cent extraction which the Bayer process gives with commercial low-silica bauxites. When high-silica bauxites were treated by the Bayer process, the amount of alumina recovered was as low as 70 per cent or less. The Combination process is now in operation in works erected at East St. Louis, Illinois, and Hurricane Creek, Arkansas. It has been of inestimable value in extending the nation's commercial bauxite reserves and making doubly sure that there would be no shortage of alumina during the war emergency.

Alumina from Clay by the Lime-sinter Method II

By F. R. ARCHIBALD,* MEMBER AIME, AND C. M. NICHOLSON†

(New York Meeting, February 1948)

THE present paper may be considered complementary to an earlier contribution on the same subject by F. R. Archibald and C. F. Jackson.¹ It is particularly concerned with engineering and technological aspects of the operations at the Harleyville Alumina Plant during its period of operation from January 1945 to July 1946. The plant was built for and operated by Ancor Corporation, at Harleyville, South Carolina, as part of the government sponsored wartime program related to alumina production from domestic raw materials. The main purpose of the program was to secure technical and engineering data, based on actual plant experience, that might serve as a foundation for large scale production of alumina from raw materials other than bauxite. The Harleyville plant was directed specifically to treatment of clays found in very extensive deposits in the Carolinas and Georgia using the lime-sinter process developed by Ancor Corporation. It is considered that the purpose stated above has been served and this paper is to record and discuss some of the more important findings.

The main factor in location of the plant at Harleyville was the presence in that locality of a rather remarkable deposit of high calcium limestone. The clay mining operation was centered near Aiken, S. C.,

and although a rail haul of ninety miles was involved there were, at the time, factors favorable to the Harleyville location offsetting, in part, the cost of transportation of clay. There are, no doubt, locations in the general area where clay and limestone deposits may be found in closer proximity but they had not been proven up when the project was undertaken. Availability of power from the Santee-Copper development whose high tension line skirted the property; ready access to rail and highway transportation; the promise, realized in actuality, of ample supply of soft water; and availability of labor supply were other factors of importance. Moreover, the general area has the decided advantage, for this type of operation, of a mild climate.

Construction was begun in August 1943, and although stopped for a time pending review of the general situation that fall, it was resumed, albeit with less urgency, and substantially completed by the end of 1944. The total capital cost was approximately \$3,460,000. The first alumina was turned out in April 1945 and from then until the plant was closed down in July 1946, the operations followed a succession of periods of production alternating with periods in which minor alterations were made in conformity with experience. Steady improvement was made and at the time operations were discontinued it was considered that experience and the necessary engineering were in shape for removal of the remaining bottlenecks and a somewhat major revision in one section of the plant. Unfortunately this could not be carried out and it was necessary to discontinue the

Manuscript received at the office of the Institute December 22, 1947. Issued as TP 2390 in METALS TECHNOLOGY, June 1948.

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¹ References are at the end of the paper.

project short of final proof that it is sound in peacetime as well as provision against emergency. A general view of the plant is shown in Fig 1.

THE PROCESS

In the Ancor[®] process, applied to clay, limestone and kaolin are mixed and fired until silica has been converted to dicalcium silicate, and alumina³ to calcium aluminates. The sintered mixture is leached with a solution of sodium carbonate and filtered. The filtrate containing sodium aluminate is agitated with a silicate-seed charge to reduce the silica content of the solution and then refiltered. Alumina trihydrate is then precipitated by carbon dioxide and, after filtration, fired until converted to alumina.

PROPORTIONING RAW MATERIALS

Clay, containing kaolin, which for calculation purposes may be represented by the formula $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$, contaminated with more or less silica or silica sand, compounds of iron and titanium and other minor impurities, is purified if necessary, by washing or other mechanical means. High-grade calcium limestone, CaCO_3 , is ground to suitable fineness and the clay and limestone are wet-blended in the proper proportions to:

1. Convert all SiO_2 to dicalcium silicate.
2. Convert all Al_2O_3 to calcium aluminates of mixed composition but approximating a proportion of 1.5 mols CaO per mol Al_2O_3 .
3. Convert minor constituents in part to ferrites, titanates, phosphates, and the like. These compounds are irregular in formation and composition and, if present in minor amounts, are disregarded in the calculation of proportions. Unless $\text{Fe}_2\text{O}_3 + \text{TiO}_2$ exceeds 4 pct of the mixture they can be provided for by increasing the $\text{CaO}/\text{Al}_2\text{O}_3$ ratio to 1.7. For operation with fairly uniform raw materials, this method of calculation permits simpler routine analytical control. For more exact laboratory test



FIG 1—PANORAMIC VIEW OF THE PLANT.

work, it is recommended that TiO_2 be allowed for as $\text{CaO} \cdot \text{TiO}_2$ and Fe_2O_3 as $(4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3)$.

It might be noted at this point that two technical papers have already appeared covering investigations contemporary with

area represent calculated sinter compositions using pure kaolinite and calcium carbonate as starting materials, using a constant ratio of 2 mol CaO per mol SiO_2 , and varying the $\text{CaO}/\text{Al}_2\text{O}_3$ ratio from 1.0 to 2.0.

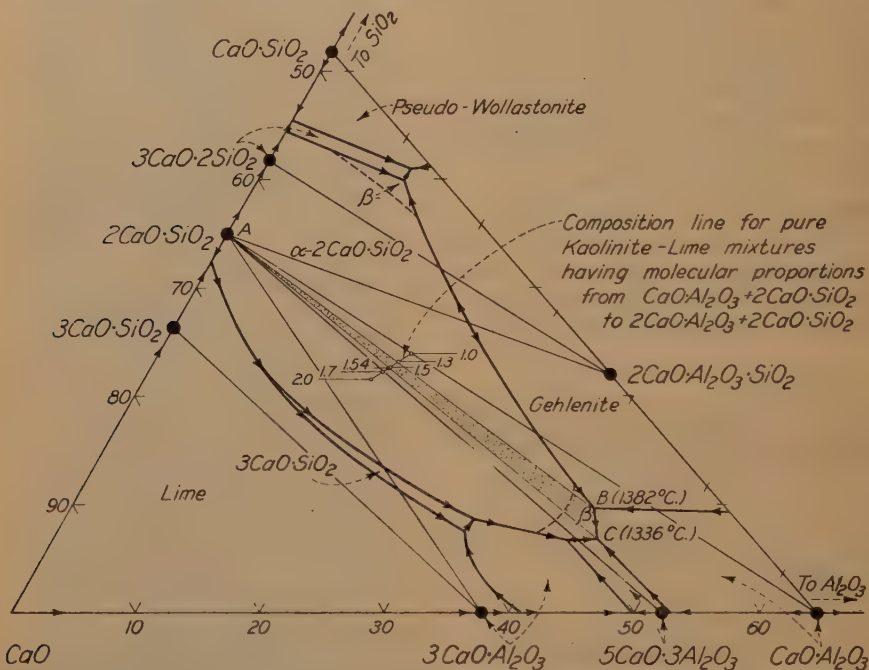


FIG 2—A PORTION OF THE EQUILIBRIUM DIAGRAM OF THE SYSTEM $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ WITH SHADED AREA SHOWING PREFERRED SINTER COMPOSITION LIMITS. (Diagram based on that of R. B. Sosman and Olaf Anderson.)

and closely related to the lime-sinter process as applied at Harleyville. Since Grim and his associates at the Illinois Geological Survey,² and Flint, Wells and associates of the National Bureau of Standards³ have covered the subjects of proportioning, influence of minor constituents, and sintering requirements with data and conclusions generally in agreement with our own findings, the reader is referred to their papers for more detailed discussion. Suffice it to say here that the composition of properly fired sinter resulting from well-blended materials will lie in the shaded area of the $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ diagram, Fig. 2. Points on the line drawn across this shaded

Both clay and limestone should be checked for phosphates and magnesia as both compounds are very detrimental. Phosphate adversely affects decrepitation of sinter and reduces alumina extractability. The presence of magnesia lowers alumina extraction, although like iron it seems to accelerate the decrepitation rate. Unless the percentage of iron is greater than about 3 pct it is not harmful, nor is the presence of sulphate in amounts up to 1 pct of SO_4 . The sulphate content is of consequence in the subsequent desilication operation but is not detrimental.

One point upon which there has been some disagreement in published papers is

that relating to the best proportion of $\text{CaO}/\text{Al}_2\text{O}_3$ for maximum extractability of alumina. Our own data support the sufficiency of 1.5 CaO per mol Al_2O_3 or even lower for pure raw materials. This is illustrated in Fig 3 and 4 and the supporting data also led to limitation of the shaded area in Fig 2.

Fig 3 and 4 are based on laboratory tests using precipitated CaCO_3 and clay of composition shown under B in Table 1. The heat treatment differed from that reported by others in that it was carried out in two stages approximating the conditions obtaining when a two kiln arrangement, described in more detail below, is used. In effect it resembled the combination of sintering and annealing described by Flint, Wells et al.³ The composition of raw

TABLE 1—Composition of Raw Materials^a

	A	B	C	D
SiO_2	45.60	45.60	2.53	1.64
Fe_2O_3		1.73		
TiO_2	2.50	1.23	0.60	0.54
Al_2O_3	36.86	37.04	0.61	0.51
P_2O_5	0.04		0.12	0.15
CaO	0.45	0.0	52.74	52.98
MgO	0.20	0.1	0.83	0.82
SO_3			0.14	
Na_2O	0.18			
K_2O	0.07			
Ignition loss.....	13.80	13.84	42.34	42.83
CaCO_3			93.88	94.67
Net CaO^b			47.46	49.44

^a Key to Table 1:

A. Plant washed clay, storage thickener, December 1944 to June 1945, average.

B. Aiken white clay, untreated.

C. Limestone, average from stockpile to June 1945.

D. Limestone, average from 12 drill holes in Harleyville plant pit.

All analyses on dry basis (110°C).

^b Net CaO = total CaO , less allowance for silica and alumina in limestone on basis of $2\text{CaO}\cdot\text{SiO}_2$ and $1.7\text{CaO}\cdot\text{Al}_2\text{O}_3$.

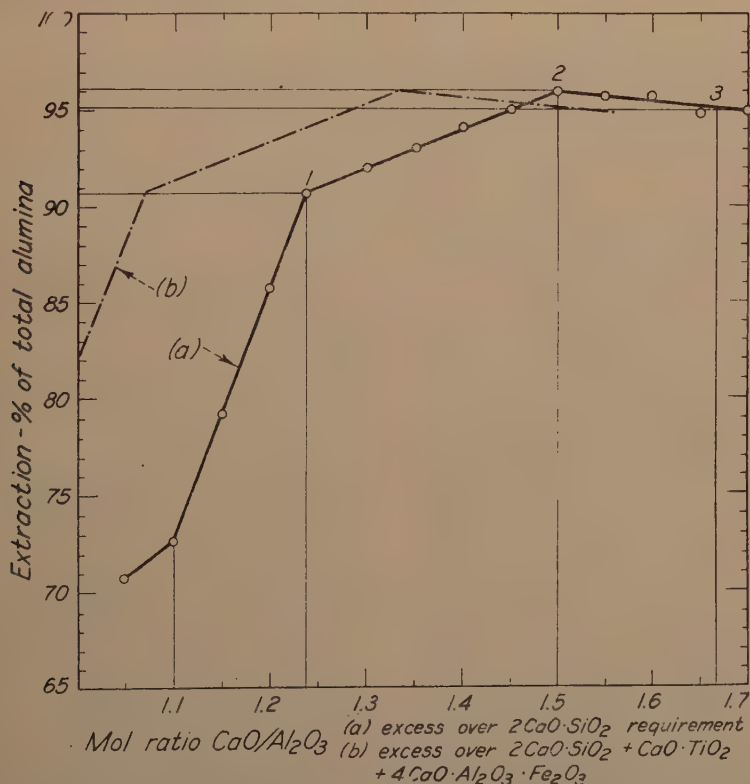


FIG 3— $\text{CaO}/\text{Al}_2\text{O}_3$ RATIO VS. PERCENTAGE OF TOTAL ALUMINA EXTRACTION FROM CLAY— CaCO_3 SINTERS.

materials used in the Harleyville plant is also shown in Table 1.

On the basis of allowance for titania and iron as well as silica and for Al_2O_3 at 1.5

made to the publication by Bogue.⁴ Insofar as calcium aluminate compounds are concerned the practical requirement is shown in Fig 3. It is with respect to the behavior of

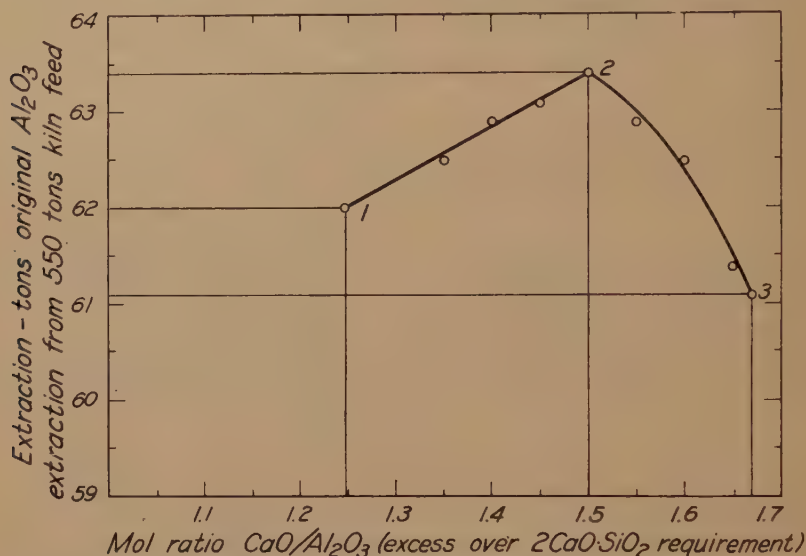


FIG 4—TONS ALUMINA EXTRACTED FROM CONSTANT WEIGHT OF KILN FEED VS. MOL RATIO $\text{CaO}/\text{Al}_2\text{O}_3$.
(Calculated on basis of data from Fig 3)

mols CaO per mol Al_2O_3 , the materials shown in Table 1, A and D would be blended in the proportion of 2.40 tons limestone per ton of clay.

Intimate mixing of the clay and limestone is essential. Results from dry blending even when the materials were ground together were never as satisfactory as from mixtures prepared by wet grinding. Dispersed clay slurry yielded better results than undispersed clay of equivalent grade.

HEAT TREATMENT

The heat treatment of raw mix to produce satisfactory sinter, the reactions involved, and the possible phases developed are so similar to those attending manufacture of Portland cement that the subject is not enlarged upon here except to point out and discuss the difference in desired end products. For a detailed discussion of reactions and possible phases reference is

dicalcium silicate that the chief differences arise in objective and technique when heat treatment for cement clinker formation is compared with that for lime-sinter formation. This aspect is considered worthy of some enlargement.

In sintering limestone-clay mixtures the work involves (1) driving off all free and combined water, (2) driving off carbon dioxide, (3) conversion of all SiO_2 to properly developed β -dicalcium silicate, and (4) conversion of Al_2O_3 to calcium aluminates $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$ and $\text{CaO}\cdot\text{Al}_2\text{O}_3$. Although the proper maturing temperature varies with the purity of the raw materials and the rate of heating, it is in the neighborhood of 2400°F and between the practical limits of 2372 and 2480°F . It is between these temperatures that the proper phases develop and excessive liquid formation, noted at higher temperatures, is avoided. The time factor required for proper matur-

ing of the desired phases when combined with the temperature limits noted, develops a combination that is difficult to achieve in the conventional countercurrent operation of a rotary kiln.

The tandem kiln arrangement shown on the flowsheet in the earlier paper was the device adopted, on the basis of pilot plant experience, to permit a longer maturing period within the required temperature limits, than could be attained in one kiln fired countercurrently. Experience with this design will be dealt with in a later section of this paper. It is mentioned here to illustrate a principle.

The necessity for annealing or maturing period had been shown in our laboratory and pilot plant work and has been verified through independent work by Flint, Wells and associates at the Bureau of Standards.³ The importance of the annealing time is related not only to formation of the desired calcium aluminate compounds which appear to involve slower reactions than silicate formation but also to completion of the crystallization of dicalcium silicate and other components. In consideration of both factors, a report by R. E. Grim and W. F. Bradley on petrographic and X ray examination of our sinter is of interest. It has been noted that sinter which decrepitated to pass 65 mesh often contained, in addition to the extremely fine decrepitation product (minus 5 microns), a variable percentage of much coarser particles (minus 65 plus 325 mesh). It was further noted that little, if any, alumina extraction could be made from this coarser fraction and that its presence with the very fine material enhanced the tendency for the entire mass to "set" during leaching, particularly if agitation was insufficient. Samples of these materials were furnished the Illinois investigators who reported the fine material as being all minus 5 microns in particle size, and composed mostly of γ -2CaO-SiO₂ and the so-called 5CaO·3Al₂O₃. The coarse material was reported

to contain abundant uninverted beta-dicalcium silicate, some γ -2CaO-SiO₂ and 5CaO·3Al₂O₃, and gehlenite in relatively large grains.

The presence of gehlenite (2CaO·Al₂O₃·SiO₂) indicates insufficiency of lime, perhaps locally in the charge because of imperfect grinding and blending or segregation in the kiln. We had other evidence of such segregation when the pulp density of slurry was low. The gehlenite is undesirable in that its alumina content is not soluble. Uninverted β -dicalcium silicate is the more serious component since it has hydraulic properties itself and also lends setting properties to the entire mass. Its presence causes mechanical troubles as well as metallurgical loss of alumina. Grim and associates report² that both gehlenite, and β -dicalcium silicate that will not invert are formed at low sintering temperatures and appear in the final sinter if either time or temperature are insufficient. They report also that the causes of non-inversion of β -2CaO·SiO₂ may be chemical due to inclusion of foreign ions (phosphate for example); or physical, characterized by fine particle size. They show that such physically inhibited β -2CaO·SiO₂ is formed when sintering time or temperature is insufficient.

We learn from other investigators⁵ that this undesirable physical condition can result from overheating as well.

In firing mixtures of requisite composition to a temperature at which the desired reactions take place in a reasonable time, there is unavoidably a proportion of liquid formed. When such liquids are cooled rapidly or quenched they form glass with high alumina content (and iron if present) and do not decrepitate. Lerch and Brownmiller give compositions and other data on such glasses.⁶ The same authors describe how such glasses may be annealed at temperatures below their melting point to yield crystalline products which "dust" on cooling due to inversion of the β to γ -dicalcium silicate.

By consideration of our own findings, and substantiation by the work to which references are made, it is clear that a two-stage kiln arrangement is fundamentally sound for production of sinter that will decrepitate completely, be free from unnecessary cementing material, and carry well developed aluminate compounds that extract well. The guiding principles are: (1) to avoid kiln temperatures above those at which a minimum of fusion takes place, and (2) to hold the charge at a temperature just short of liquid formation for as long a time as necessary to complete the desired reactions.

In the light of these observations the logic of a tandem kiln arrangement is clear. In conventional countercurrent kiln firing a sharp peak in the material temperature curve is unavoidable. Such a sharp peak is desirable in Portland cement manufacture as it is desired to avoid complete crystallization and dusting because of dicalcium silicate inversion. In preparation of sinters for alumina extraction the opposite condition is necessary for best results.

The temperature to which the charge in the preheat kiln should be heated is determined in large measure by the balance that can be obtained in operation. In the laboratory tests, using pure materials, it was shown to be preferable to preheat only to about 1400°F and then to plunge the charge into a hot furnace bringing it as quickly as possible to 2400°F. In actual operation this is difficult to accomplish because of the limit of fuel that can be burned properly in the sinter kiln. Plant operation has proved that exceptionally high quality sinter can be produced by preheating to a near-sintering temperature in a countercurrently fired kiln and by annealing in a cocurrently fired kiln.

The heat requirement for drying and sintering mixtures made from materials given in Table 1, A and D, and assuming normal fuel efficiency, exit gas temperature and radiation losses, has been calculated at

7.2 million Btu per ton of sinter when feeding slurry at 57 pct solids. This is in accord with the results of plant experience when plotted for 50 to 75 pct of rated capacity and extrapolated to full capacity.

If the sinter has been well matured in accordance with the requirements already noted, the subsequent cooling step does not require more than ordinary control. Well burned sinter dusts down rapidly within a normal cooling period. The extent of dusting and laboratory extraction that can be achieved are shown in Table 2 based on plant results for three separate 24 hour periods. The percentage of dusting was determined by screening composite cooler discharge samples through a 65-mesh screen. In operation, the oversize is returned to the kiln feed for further heat treatment. It has been shown by laboratory test that unless the oversize is badly off composition it will dust down satisfactorily after additional annealing in the proper temperature range.

TABLE 2—*Sintering Results*

Date	Operation, Hr	Kiln Feed, Dry Tons	Cooler Discharge ^a	Decrepi-tation, Per Cent (65 mesh)	Alumina Extract-able, Per Cent ^b
6/14/46	24	329	East West	99.1 99.0	83.4 84.8
6/20/46	24	363	East West	94.8 94.3	87.4 75.7
6/29/46	24	245.3	East West	96.2 98.2	97.3 81.3

^a East cooler handled lumps and West cooler pellets passing grate.

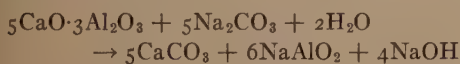
^b By standard laboratory leaching procedure.

LEACHING

The first requirement for satisfactory leaching is good sinter. By good sinter is meant that the calcium aluminates and γ -dicalcium silicate are properly developed according to the description already given. The particle size is normally a good measure of the quality of sinter. Characteristically, sizing of sinter such as that represented by

Table 2 shows the particle size of the main fraction to be of the order of 5 microns. The bulk of the remainder will be found in the plus 325-mesh fraction. The possibility and advisability of separation of the over-size fraction and its return to kiln feed is discussed at greater length under the section on operating problems. A second requirement is intense agitation in the first moments of contact between sinter and solution to prevent formation of pellets. If these first two requirements are met and the period of agitation before filtering is long enough, (up to 45 min.), the difficulties variously described as "setting up" and "gelation" can be avoided. Prior to operation of the plant it was considered best to limit the agitation time to 15 min. or less and rush the pulp through the rest of the circuit before setting up occurred. Various agents such as starch were tried in an effort to prevent the setting up but they served only to delay it.

Although the modern interpretation of "aluminate" solutions is that they are aluminum hydroxide sols stabilized by excess alkali and their behavior is in keeping with that interpretation, the familiar type of equation is useful for calculation.



In continuous leaching, the solution, returned from precipitation, becomes complex and contains in addition to sodium carbonate, alumina, silica and "free alkali." By free alkali is meant that concentration, determined by titration with acid, above that required to prevent precipitation of aluminum hydroxide. The equation indicates that a mol ratio $\text{Na}_2\text{CO}_3/\text{Al}_2\text{O}_3$ of 1.67 is required but experience shows that the ratio should be at least 2.0 and preferably 2.5. Pulp density is another important factor and for optimum mechanical efficiency, as well as good extraction, the pulp density should be from 17 to 20 pct solids. High concentration

of Al_2O_3 in pregnant solution is desirable if pressure digestion is employed for desilication, but this is not the preferred method for reasons enlarged upon later and better operation can be achieved if the concentration is reduced to 50 g Al_2O_3 per liter or less, and the soda content adjusted to suit.

The control of free alkali or caustic (NaOH) during leaching, desilication and precipitation is of prime importance. Free caustic is formed when sinter and sodium carbonate solutions are mixed (1) by carbonation of free lime, and (2) by dissolution of calcium aluminates. It also forms when alumina hydrate precipitates. It is converted to carbonate by carbonation with CO_2 during precipitation and, if desired or necessary, during leaching agitation. There must be sufficient free alkali in the pregnant solution to prevent precipitation of alumina during desilication. For pregnant solution having a concentration of 150 gpl total alkali measured as Na_2CO_3 , and 50 gpl Al_2O_3 , 20 gpl of free alkali expressed as NaOH is preferred. Since NaOH tends to dissolve SiO_2 from the sinter and does not aid in dissolution of Al_2O_3 , its concentration should be kept to the minimum required for holding alumina in solution until its precipitation is desired. Excess free alkali is also objectionable in that it aggravates the hardening and weakening of filter cloths. In plant practice free alkali in the leaching, desilication and precipitation circuit was controlled by the proper amount of carbonation in the precipitation tanks and by introduction of CO_2 to the leaching agitators. Solutions from the precipitation tanks were analyzed regularly to follow the course of precipitation in order that flue gas might be admitted at the proper rate to carbonate all of the NaOH as it forms. Still closer regulation of free alkali in the leach pulp was obtained by plant operators making regular titrations of the pregnant solution and adjusting the rate of carbonation in the leaching agitators as required.

DESILICATION

In the leaching procedure just described, no special care is directed towards preventing dissolution of silica, emphasis being placed on maximum removal of alumina. Under such circumstances the pregnant solution will contain silica approximating 2 to 3 pct of the dissolved alumina. In plant operation where recycled solutions were used it was ordinarily near the lower figure but in laboratory tests using fresh carbonate solution it approached the higher figure.

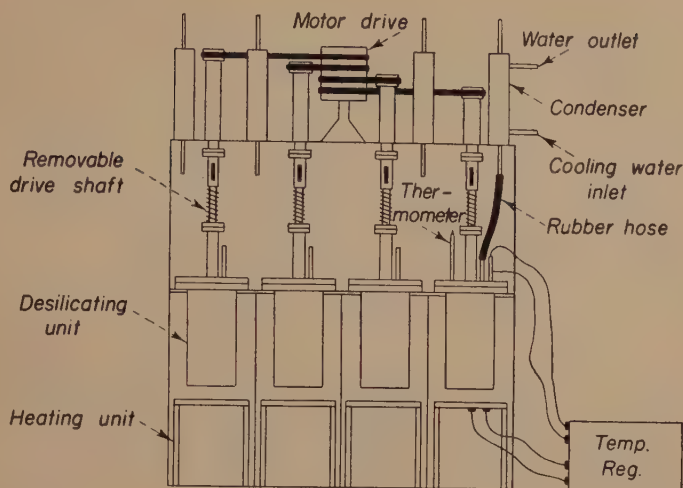
This requires that a separate desilication operation be carried out on the solution to such an end point that alumina of satisfactory grade can be recovered in the precipitation step following. Experience in the plant showed that if the silica concentration in solutions was reduced to 0.13 to 0.15 pct of the alumina content, up to 85 pct of the alumina could be recovered in any cycle with the per cent silica content about one-third of that indicated by the pregnant solution composition. By stopping precipitation at that point, preferential deposition of alumina permitted recovery of a satisfactory product (0.05 pct SiO_2 or less).

The problem then is to reduce the silica content of pregnant solution to the degree indicated.

The desilication process, as developed at the time of publication of the earlier paper, involved digestion of the solution at elevated temperatures in pressure vessels. It resembled the Bayer digestion process in temperature and pressure requirements and the mechanism of silica inactivation was probably similar. Metallurgically this process was all right but the mechanical operation, as it developed, left a great deal to be desired. This subject is dwelt on later, and here a process development in a more desirable direction is described. It is the chief development, insofar as process modification is concerned, that has come out of the Harleyville operations.

Before going into the details of technique and results, it is pertinent to discuss briefly the nature of "aluminate" solutions produced from the leaching process already described. If we consider them as aluminum hydroxide sols stabilized by excess hydroxyl ions the behavior is more understandable. Silica apparently aids in the stabilization. If the concentration of free hydroxyl ions is reduced by carbonation, a gel may be formed, or a crystalline hydrate, depending on the concentration and other conditions. Some of the silicate complexes will fit into the resulting structure and be trapped. If on the other hand, a crystalline material with a structure showing unsatisfied valences (or in other words a tendency to form bonds with the silica) is introduced, the latter may be robbed from the solution and build up on the "seed" charge. A reduction in free hydroxyl ion concentration will aid in this action but it cannot be lowered too much or the aluminum hydroxide sol will become unstable and the hydrate will come out. Another point of importance is that the seed must be as pure a species as possible. If contaminated with dicalcium silicate for example it is not as effective.

This is the viewpoint that guided the desilication tests of which the results are reported here. Space does not allow a full treatment but a few graphs are included for illustration. In considering Fig 5 to 10, the method may be kept in mind. Since solutions of this nature, like sols generally, vary in behavior with age and details of preparation and history, the test solutions were prepared individually and in a uniform manner just before use. Samples of sinter were leached according to a standard laboratory procedure as close as possible to plant procedure except that in the latter case the leach solution contains unprecipitated alumina from an earlier cycle. Confirmatory desilication tests on plant solutions showed that results were comparable to those obtained in the laboratory



4 Unit Desilicating Apparatus
showing connections for one unit.

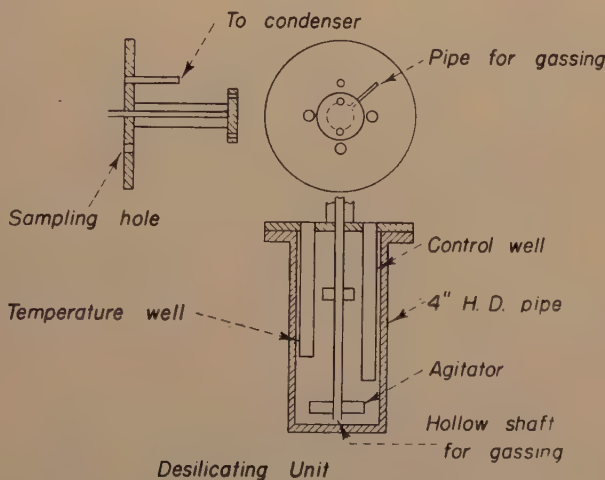


FIG 5—LABORATORY APPARATUS FOR DESILICATION.

procedure noted. The seed charge can be prepared by prolonged heating of clear

TABLE 3—Composition of Desilication-Seed Charge

Constituent	Per Cent	Constituent	Per Cent
SiO ₂	32.16	Na ₂ O	22.70
Fe ₂ O ₃ + TiO ₂	0.26	SO ₄	3.62
Al ₂ O ₃	32.10	Ignition Loss	8.00
CaO	1.18		

solutions but it was more convenient to use a sample of crystalline white mud taken from the pressure digestion tanks in the plant. The composition was as shown in Table 3.

The composition changed but little through repeated use in clear solutions except that the CaO content became less. Its presence in the starting material resulted from the use of a small quantity of

CaO in plant operation to aid in settling of the iron, precipitated when autoclaved solutions cooled, in preparation for filtering. In the new procedure the use of CaO is

of a satisfactory seed charge. This is discussed at greater length following presentation of illustrative data in Fig 5 to 10.

In general, the test procedure was to

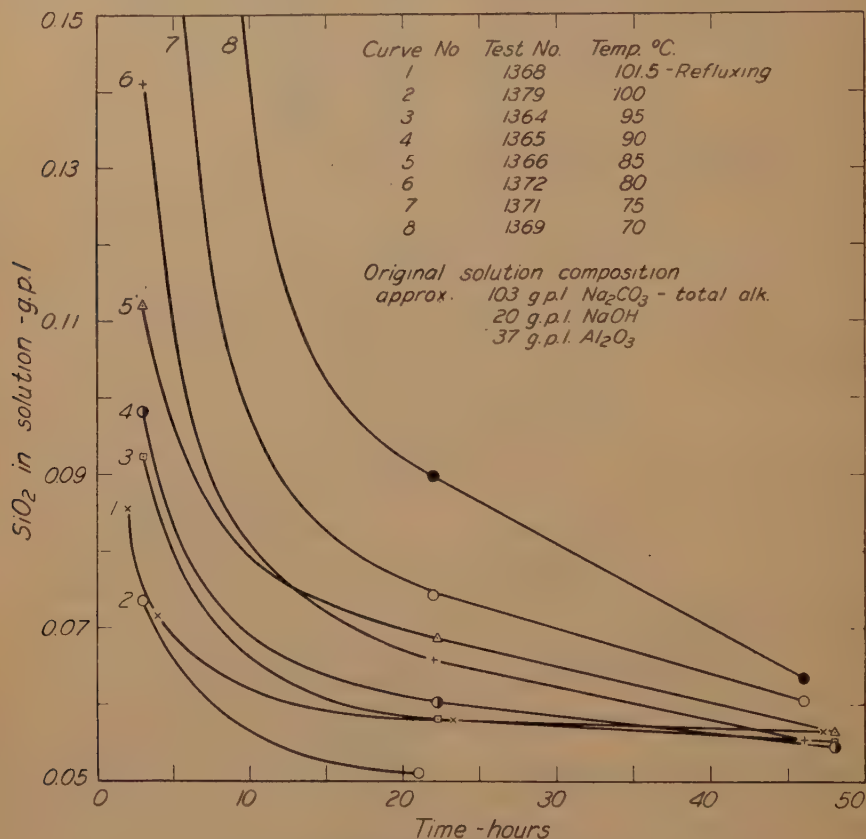


FIG 6—DESILICATION TEMPERATURES.
40 g silicate-seed charge used in each test.

unnecessary, as the iron appears to be incorporated in the white mud and its concentration in solution is reduced to a very low value. Re-use of white mud from one test as seed for following tests tended towards improvement in desilication results. The sulphate content of white mud is worthy of note. The sulphate concentration in plant solution reached 12 g Na_2SO_4 per liter, originating from the sulphur content of the fuel used in sintering. It is a fortunate circumstance that sulphate is supplied in this way since it enters into the composition

bring 1200 ml of solution to the desired temperature, with stirring, and add the dry seed charge. Check tests had shown that an undried seed charge, produced in an earlier run, yielded results comparable to those when the seed was dried. For ease in addition and to avoid dilution, dry charges were then used. An electronic temperature control device permitted close regulation of this variable. Silica determinations on solution were made colorimetrically. In this connection it is noted that great care was taken in calibrating the instrument

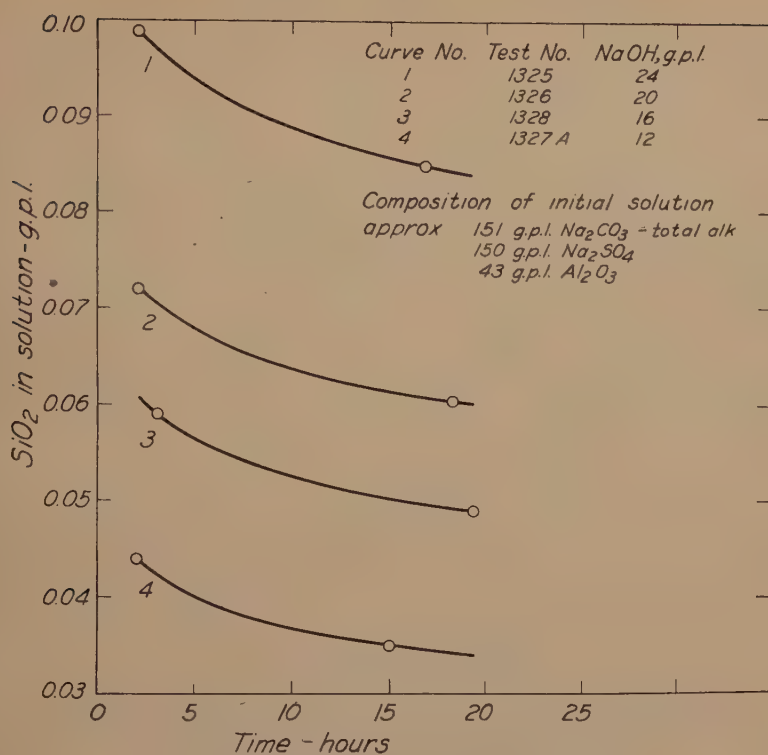


FIG 7—EFFECT OF NAOH CONCENTRATION.
 40 g of silicate-seed charge used in each test.

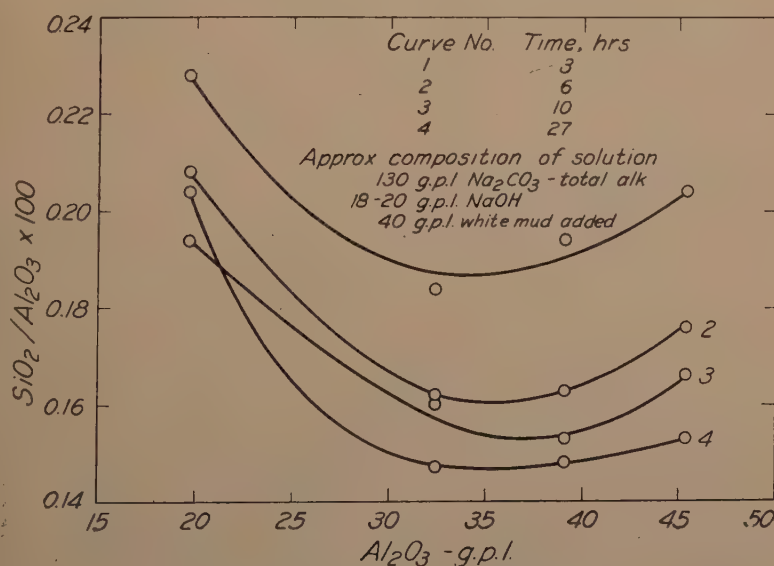


FIG 8—EFFECT OF Al_2O_3 CONCENTRATION.

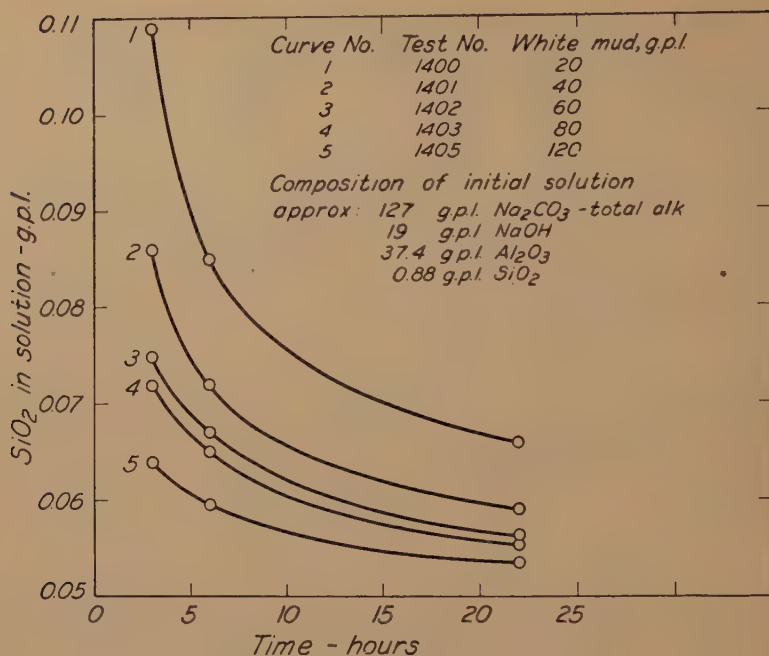
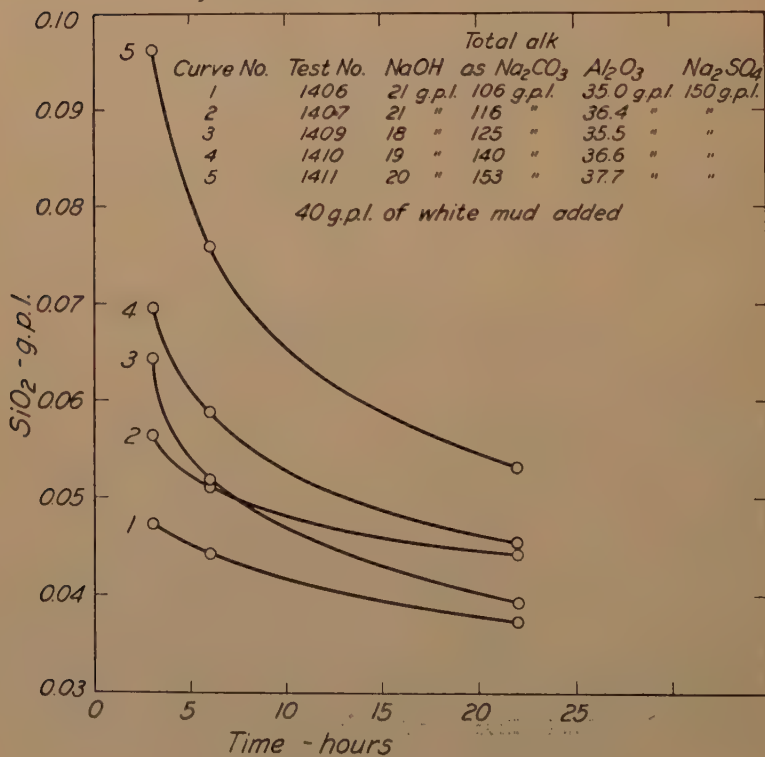


FIG 9—EFFECT OF WHITE MUD CONCENTRATION.

FIG 10—EFFECT OF Na_2CO_3 CONCENTRATION.

and unless gravimetric determinations on such solutions are done with exceeding care they show lower comparative results than those reported.

The significance of the results will be obvious from the figures. Although the solid desilication product has been called "white mud," through usage of the term as comparable to the "red mud" residue from the Bayer process, it is a misnomer insofar as the physical nature of the product is concerned. The products are crystalline, and easily filtered and washed. A typical sample was examined for us by Drs. Grim and Bradley of the Illinois Geological Survey who reported that the "chief phase is a cubic material of the sodalite group, a lattice-cell size between sodalite and noselite and a refractive index of 1.48 which is consistent with that of a low sulphate noselite."

Reference is made to the work of investigators at the Bureau of Standards who pioneered in the use of prepared seed charges for removing silica from aluminate solutions and who have summarized the pertinent literature. The work reported in this paper differs in that: (1) The seed is prepared by simply heating the silica-rich aluminate solution, which from the nature of earlier steps in the process, contains some sulphate. As the cycles are repeated the seed charge increases in quantity and efficiency. (2) Temperatures below the boiling point of the solution are effective. These differences are of practical importance in making for simplicity of design and operation, and heat economy.

PRECIPITATION AND CALCINATION OF ALUMINA

The subject of precipitation of alumina as trihydrate from alkaline solutions by carbon dioxide requires no enlargement for the purposes of this paper except to note that it can be carried out successfully by continuous precipitation in modified Dorr agitators. Temperature control is not a

critical factor within reasonable limits but the rate of precipitation is of prime importance. A more uniform product of desirable particle size is obtained if precipitation is rapid and a minimum of fines are returned to the precipitators. It appears that in this method it is undesirable to encourage auto-precipitation or to depend on growth of fine seed hydrate to obtain suitable particle size. Calcining the hydrate presents mechanical problems but the chemistry is simple enough.

In review of the process as described in the earlier paper and modified through experience according to the discussion already given, a flow sheet is included here, (Fig 11). The modifications of consequence relate to desilication, and the inclusion of an air separator to effect more complete removal of imperfectly developed sinter.

A material balance for the process, based on plant experience, and projected to full rated capacity of 50 tons alumina per day is given in Table 4.

ENGINEERING AND OPERATION

Original design, operating experience and modification, or plans for modification are so clearly related that the ensuing discussion will incorporate all three under headings based on a division following the sequence of operating steps, as follows: mining, clay washing, milling, sintering and screening, leaching, desilication, hydrate precipitation and calcining.

Mining

Clay mining presented no problems other than those attending the use of second-hand hauling equipment. In preparation of the pit 34,000 cubic yards of overburden were removed on contract at a cost of \$0.198 per cubic yard, uncovering 67,000 tons of minable clay. It was estimated that future stripping, to be done in conjunction with the mining operation,

would cost \$0.058 per cubic yard. This estimate as well as all other estimates given in this paper are computed on the basis of costs prevailing as of March 1946. A total

the cost has been estimated at \$1.02 per dry ton. These costs are given as a prelude to the discussion of economic considerations in the following section.

TABLE 4—*Material Balance—50 tpd Al_2O_3 —Ancor Process*

Material, Unit	Clay Washing		Limestone Milling		Sintering		Leaching	
	Per Day	Per Ton Al_2O_3	Per Day	Per Ton Al_2O_3	Per Day	Per Ton Sinter	Per Day	Per Ton Sinter
Raw clay, tons.....	187	3.74						
Washed clay, tons.....	159	3.18						
Limestone, tons.....			384	7.68				
Quebracho, tons.....	0.374	0.0075						
Caustic soda, tons.....	0.561	0.0112						
Sinter, tons.....					357		357	
Residue, tons.....					357			
Leach solution, tons.....								
Soda ash, tons.....							4	0.0112
Coal, tons.....					89	0.25		
Power, kwh.....	4,400	88	7,600	152	7,800	22	5,000	14
Steam, lb.....							132,000	369.7
Water,* gal.....							90,000	252.1
Oil, gal.....								
Labor, man-hr (incl. maintenance)....	35.9	0.718	35.9	0.718	55.8	0.156	58.4	0.164
Materials and supplies, dollars.....	2.64	0.053	30.54	0.611	89.20	0.250	30.00	0.084
Alumina, tons.....								

* All fresh water used for cooling flue gas and washing filters.

TABLE 4-a—*Material Balance—50 tpd— Al_2O_3 —Ancor Process*

Material, Unit	Desilication		Precipitation		Calcination	
	Per Day	Per Ton Sol'n	Per Day	Per Ton Al_2O_3	Per Day	Per Ton Al_2O_3
Raw clay, tons.....						
Washed clay, tons.....						
Limestone, tons.....						
Quebracho, tons.....						
Caustic soda, tons.....						
Sinter, tons.....						
Residue, tons.....						
Leach sol'n.....	1,380		1,380			
Soda ash, tons.....						
Coal, tons.....						
Power, kwh.....	2,800	2	7,100	142	3,500	70
Steam, lbs.....	228,000	165.2			48,000	960
Water,* gals.....	8,000	5.8	302,400	6,048	13,000	260
Oil, gals.....					1,500	30
Labor, man-hrs. (incl. maintenance)....	58.4	0.043	58.4	1.168	37.2	0.744
Materials and supplies, dollars.....	21.50	0.016	20.00	0.4	22.00	0.44
Alumina, tons.....					50	

* All fresh water used for cooling flue gas and washing filters.

of 21,850 tons of clay were mined with an average moisture content of 18.6 pct. On the basis of a selected five day period, and including stripping, mining, hauling to the loading pit, freight, and unloading to the stockpile at Harleyville, clay cost \$1.24 per dry ton at the plant. For steady operation

Limestone mining did present some unexpected problems related to the unusual physical character of the material. After some experimenting a procedure involving a minor amount of blasting, loading with dragline bucket, and hauling from pit to stockpile with 13 yard, rear dump Diesel

trucks was employed. For an established plant, and in consideration of the softness of the rock and the fact that the deposit of

month (February 1946) averaged \$0.347 per ton, delivered to the plant stockpile, (dry basis). Moisture as mined was ap-

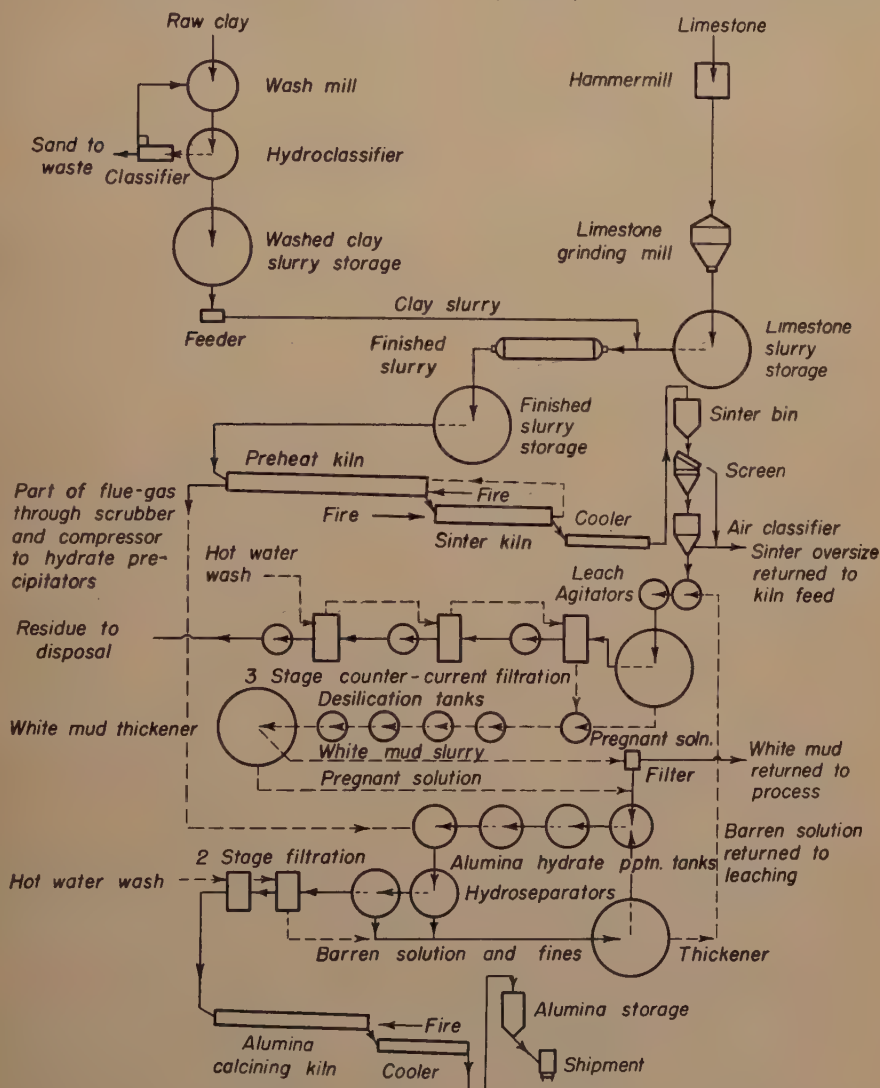


FIG 11—FLOWSHEET OF ANCOR PROCESS.

satisfactory material is uniformly about 60 ft thick, more economical methods could be devised. Overburden of 86,000 cubic yards was stripped from the pit and access road, making available for mining some 165,000 tons of limestone. Direct operating cost excluding stripping, for a selected

proximately 22 pct. The chemical analysis is given in Table 1.

Clay Washing

The clay washing operation obviated the necessity of selective mining. It was operated periodically as required. Crude clay

was blunged in a wash mill at 40 pct solids using 6 lb caustic soda and 4 lb quebracho extract, (35 pct tannin), per ton of dry clay, as dispersing agent.

tion are illustrated in Table 5. The laboratory results show the separation and efficiency possible. It is expected that in time plant performance would have equalled it.

TABLE 5—*Laboratory Washing Results on Typical Aiken Clays*

Sample	Pulp Properties			Products	Weight, Per Cent	Analysis, Per Cent	
	Solids, Per Cent	Viscosity (Water = 1)	pH			SiO ₂	Al ₂ O ₃
A	39.5	1.078	10.20	Raw clay	100.0	48.60	34.60
				Washed clay	91.3	44.76	37.68
				Sand	8.7	92.0	2.28
B	40.6	1.050	10.35	Raw clay	100.0	58.60	27.10
				Washed clay	68.5	45.00	30.36
				Sand	31.5	89.48	5.86

The silica sand settled out in a 75-ft diam classifier with thickener rake mechanism and was cleaned in a 25-ft diam hydroclassifier, the overflow of the latter returning in closed circuit to the wash mill. The 75-ft classifier overflow, (finished clay slurry), at 37 to 38 pct solids was stored in a tank 110 ft in diameter with a capacity of 1900 tons of clay (dry equivalent). The cost of clay washing was \$0.63 per ton of dry crude clay.

A pulp density control device used in conjunction with the wash mill, keeping the density at 40 pct, proved indispensable in regulating the entire clay washing operation. In early operation using the method described, difficulty was encountered in getting the sand to settle out in the large diameter classifier, although samples taken from the tank and poured into a beaker would classify immediately. It was recognized that a measure of gel structure must have developed in the large tank, entrapping the sand particles, although the viscosity of the mixture, on removal from the tank, was little more than that of water. A remedy was found in circulating the upper 10 ft of the 75-ft tank by means of a pump, spraying it back over the surface in such a way as to maintain the downward movement of the pulp as well as a slight swirling motion. Results of the clay washing opera-

Sample A in Table 5 represents average clay mined and Sample B typifies low grade sandy clay. In each case caustic soda and Quebracho extract were used as dispersants in amounts equivalent to 6 and 4 lb per ton of dry clay respectively. The sand product from A was 82 pct, and from B 89 pct minus 325 mesh. The efficiency of free silica removal was 98.2 and 94.2 pct in the respective cases.

In the plant operations alumina recovery of 97.6 pct, and weight recovery of 93.4 pct were achieved using the same pulp conditions and reagents as noted above.

In consideration of these results it should be noted that the sand particles are very fine and also that the general type of clay used is considered difficult to disperse. The combination of reagents used accomplished the dispersion without difficulty.

Milling

It was in the milling department that the first serious snags were struck, and the experience in circumventing them may be of interest. The difficulties stemmed from the ability of the freshly mined marl-like limestone to hold water and pack together when crushed. This behavior is not so evident when the material has lain about in lumps exposed to air and weather. The original design of the milling section pro-

vided for dry crushing in a hammer mill followed by storage in a bin and dry feeding to the primary ball mill. It had been based on the properties and behavior of material taken from an old unused quarry, and that had been exposed to the weather. It is considered that the important thing to record in this case, and in others following, is not the miscalculation or the troubles it caused, for they will be fairly obvious, but the manner in which they were circumvented without requirement of a major change in design or equipment. The first answer was to add water to the hammer mill and make this a wet operation. This was simple enough in itself and effective. It necessitated a chain of related readjustments of flowsheet, however, and demanded a change in the clay treatment section as well. It was now necessary to measure the limestone as a slurry as well as the clay, and to keep the pulp density of the latter to a maximum to avoid undue dilution of the final blended slurry. The flowsheet that then developed involved wet crushing in the hammer mill, yielding a pulp at about 70 pct solids, which was then ground without further dilution in the primary ball mill (open circuit), and stored in the slurry tanks that had been originally designed for finished slurry storage. The desanded clay slurry at 37 to 40 pct solids, and the limestone slurry at about 70 pct solids were then proportioned out from the respective storage tanks by a Richardson solution scale, modified to handle slurry. The scale weight settings and dump timing were adjusted by the operator to suit the pulp densities of the respective slurries. Further adjustments of weight settings were made to suit limestone-to-clay ratios determined by the laboratory from chemical analysis. The two slurries, yielding a mixture of 57 to 58 pct solids, were then ground together in the 5-ft diam by 22-ft tube mill, and pumped to the feed end of the preheat kiln. The new scheme was workable and was used throughout the

period of operations. The chief drawback was the lack of finished slurry storage, to iron out irregularities in the feed rate and composition. This provision would have been simple enough and was planned for, had the project been continued.

Sintering

The need for a two-kiln combination has been dealt with, in principle, under the discussion of the process. Mechanical interpretation of this need was a step into unfamiliar territory. Pilot-plant experience had shown that a kiln with the direction of firing parallel to material flow offered real advantages in prolonging the maturing period within a temperature range, restricted on the one side by liquid formation and resulting sliding and balling of the charge, and on the other by improper development of the desired phases. Whether or not equivalent prolongation and control of the reaction zone could be accomplished in two, or even one, countercurrent kiln is left to the opinion of the reader. The difficulties and outcome of the countercurrent preheat and cocurrent reaction kiln combination are our concern in this paper. The two main principles influencing design and operation of this sort of kiln arrangement, that were not appreciated in the first place, were: (1) in order to balance the heat input into such a system, it is necessary to provide for firing into both kilns, and (2) the slope of a cocurrently fired kiln should be much less than is customary in countercurrent kilns. These answers were evident only after disheartening experience with poor combustion of fuel, sinter balls and rings, failure of refractories, and irregularity of sinter quality. The troubles were largely eliminated by correction in the two directions noted. Firing was provided for in the preheat kiln as well as in the sintering kiln. This did not increase the overall fuel consumption and relieved both attack on refractories and tendency to form serious

rings and balls. Best operation was obtained when the preheating brought the charge close to sintering temperature, thereby reducing the heat input requirement to the sinter kiln. The slope of the sinter kiln was not easily changed from the $\frac{1}{2}$ in. per foot original slope, but a fairly equivalent effect was obtained by building a high dam at the discharge end.

The original design provided for filtering of the raw slurry but the change in milling flowsheet and nature of the slurry made this impractical and slurry at 57 pct solids was fed directly to the kiln. A network of chains was added to the preheat kiln in conformity with this procedure. The induced draft fan capacity proved inadequate to handle the increased gas volume at full rated kiln capacity, and this limitation to a maximum of 70 pct rated capacity was not removed at the time of shut-down. The preheat kiln was 9 ft 6 in. in shell diameter and 250 ft long; the sinter kiln 11 ft 6 in. by 85 ft; and the return flue from sinter kiln discharge to preheat kiln was 8 ft in diameter. The speed of both kilns was variable.

The sinter was cooled in an 8-ft diam by 48 ft multitube indirect cooler and no trouble was encountered in this operation except for the limitation of size of lumps entering the cooler. A heat-resistant alloy grate was later added at the kiln discharge and an auxiliary cooler installed to take the lumps that would not pass the 3 in. spacing of the inclined grates. The latter cooler was of simple cylindrical shell type in which had been set a section of breaker liners, a grate and angle bar lifters. The later operations gave promise of elimination of oversize sinter lumps entirely.

Double deck Hum-mer screens were used for separation of the cooled sinter at 50 mesh. Early trouble in getting the fine material to pass the screens was remedied by use of sandwich-type screen in which the fine screen was backed by one of coarser mesh. The reasons for failure of the ordi-

nary type of screen and success of the special type were not obvious.

It has been found of great advantage to make the size separation on sinter at a much finer particle size than is possible with a screen. The sinter is particularly well suited for air separation since, when properly burned, it breaks down spontaneously by decrepitation to yield particle sizes nearly all in the order of 2 to 5 microns. Improperly burned sinter does not break down to such fine sizes and appears mainly as plus 325-mesh particles. There is such a wide difference between the particle size of what would be rejected and the finished portion that an air separator is very efficient. It is highly desirable to remove and re-fire the plus 325-mesh sinter because extraction of alumina is poor for this oversize, and returning for another pass through the kiln will correct it. Moreover, if this oversize passes on into the leaching operation it tends to settle out in agitators and filter wells and promotes cementing of fine and coarse material. Therefore, it is now proposed to screen sinter at a much coarser size (probably 20 mesh) and follow the screens with an air separator. The oversize from both screen and air classifier would return by a conveyor belt to join the feed to the sinter kiln.

Leaching

The general scheme of the leaching plant, involving two stages of agitation followed by three stages of countercurrent filtration, proved satisfactory. Each stage of filtration was, in reality, composed of two stages through separation of filtrate and wash solutions and the use of the more dilute solution from each filter as repulping liquid in the stage preceding. Thickeners were avoided in the design through fear of setting-up tendencies of the pulps. It has been explained that this tendency can be practically eliminated by provision of adequate agitation intensity at first contact of solution and dry solids, and elimination of

plus 325-mesh sizes from sinter. The total agitation time should be longer than that reported earlier as sufficient. Since very intense agitation is a relatively expensive operation, the use of milder agitation followed by mild open-circuit ball-milling would be considered for design of a new plant. Laboratory tests have shown that this is a satisfactory procedure. Control of pulp densities, temperature, and free alkali concentration during leaching were important factors but presented no difficulties. Free alkali concentration was regulated by blowing scrubbed flue gas (at 20 lb pressure) into the agitators. Additional agitation and aid in precipitation of colloidal iron was achieved by aerating the solutions during leaching.

The leaching operation was not without its measure of problems, the chief of which was the matter of filter cloth. Various types of cloth were tried, including treated cotton fabrics and such synthetic and metal cloths as were available in wartime. The most economical in use was untreated cotton cloth, although it had to be replaced frequently on the first stage filters. These were replaced after 3 days operation on the average, the second stage after 10 days and the third stage after 30 days. Laboratory tests indicated that nylon cloth would be very satisfactory, and in the pilot-plant work multipore rubber cloth had been used with good success. Neither was available during the period of operations. Through removal of the chief causes of the setting or cementing properties of leach pulps in the manner already discussed, the use of a thickener for the first stage of solution replacement is considered feasible and provides a second alternative for relieving the first stage filtering problem.

Because of intermittent operation and cumulative limitations that have been described, the best leaching extraction appearing on the plant records for a 24-hr period was 75.6 pct, and for an 8-hr shift 77.6 pct. In the latter case the sinter con-

tained 16.13 pct Al_2O_3 , the residue 3.62 pct alumina and 0.57 pct Na_2O . Residues with soda content as low as 0.33 pct Na_2O were obtained.

Desilication

The use of pressure vessels and temperatures above the atmospheric boiling point of the solutions as a desilication procedure is now considered obsolete insofar as the process under discussion is concerned, and the operating troubles connected with it will not be dwelt upon. As noted before, the silica content of solutions could be reduced to satisfactory values but mechanical troubles made the operation troublesome, irregular in performance, and costly.

The revised procedure already described would be interpreted in operation by the use of covered and heat-insulated agitators of conventional design, followed by a thickener, and for safety, a filter for final clarification of the overflow. The silicate product, represented by the thickener underflow would, in part, be circulated as seed charge, and in part be filtered with the overflow or returned to the leaching filters.

Hydrate Precipitation and Calcination

The equipment and its arrangement for these operations were suitable and generally satisfactory. Some minor changes in pipe fitting were made and, as would be the case in any industrial development, the arrangement in a future plant would not be quite the same. The use of Dorr-type agitators for precipitation of hydrate was a departure from custom in alumina plants. On the basis of experience at Harleyville their use can be recommended when precipitation is effected by carbonation.

Another departure of consequence was in the elimination of evaporators. This not only avoids expensive equipment and operation but also eliminates a common source of scale and plug-up troubles. The need for evaporators was eliminated by the efficiency of multi-stage countercurrent filtra-

tion, careful regulation of wash water, and elimination of water gland pumps except in special cases.

No attempt was made to produce metal from the alumina produced in the Harleyville plant. The entire production was disposed of to users in non-metallic industries. Metal grade alumina was made for short periods but it was not possible to maintain this grade on account of mechanical and design limitations that have been noted.

Analysis of alumina produced in the Harleyville plant is shown in Table 6.

ECONOMICS

That clay deposits, of grade comparable to that treated in the Harleyville plant, are very extensive and strategically located need not be enlarged upon here. The deposits found in the general area, of which the Aiken properties are a part, extending roughly from Columbia, South Carolina to Macon, Georgia, are probably the largest; but other areas have received attention in alumina project studies and still others are well known. The ultimate reserves of suitable clay can, for practical

TABLE 6—Analysis of Alumina Produced

	Average 1000 Tons	June 1946 Average 231 Tons	Good Shift Results ^a			
			Calcined Alumina		Hydrate	
			a	b	c	d
Al ₂ O ₃	98.10	98.21				
SiO ₂	0.32	0.28	0.125	0.10	0.02	0.03
Fe ₂ O ₃		0.033	0.042	0.004	0.02	0.004
Na ₂ O.....		0.60				
Loss on ignition.....		0.53	1.45	0.51		
Screen size, +100.....		1.59	1.84	1.50	1.38	1.22
+200.....		39.07	70.98	47.38	43.00	41.80
+325.....		71.13	94.58	84.60	80.06	67.20

^a a, b, c and d represent individual 8-hr shifts selected from plant records for illustration.

Early operations were beset with difficulties that were overcome partly through operating experience and partly through alterations of flowsheet or equipment. It was in the last four months of operation that the results of accumulated experience began to show up in rapid improvement. Although the project was discontinued before the corrective changes necessary for final proof could be made, it is firmly believed that the process, as represented by the flowsheet already given (Fig 11), is sound, workable, and could be an economic success at the present time in a well-located and well-engineered plant. It was further estimated that from 9 months to 1 year of further operation would be required to reach the objective of 50 tons alumina per day and bring each step to satisfactory efficiency. The general economic aspects are dealt with in the following section.

purposes, be considered unlimited. The reserves tributary to the Harleyville plant, (Aiken, S. C. and adjacent Georgia), are estimated at 50 million tons. For this local area alone, at 33 pct alumina content in the clay, the Al₂O₃ equivalent is equal to the entire United States reserves of bauxite down to a grade of 30 pct Al₂O₃, as reported in 1945.⁶ If the total reserves in the Carolinas, Georgia and Alabama are considered, the estimate goes beyond reasonable comparison. If the other extensive clay deposits in the United States are also considered the total tonnage of raw material dwarfs all others that might be considered, including foreign as well as domestic bauxite.

Such enthusiastic statements are not new and inevitably lead to discouragement of the proponent on the basis of costs, both capital and operating. It is admitted that

on the basis of performance in terms of actual cost per ton produced, the Harleyville plant record supports the discouragement. On the other hand the Harleyville experience has supplied factual data for most of the cost elements, and assuming that the design improvements briefly noted in this report would successfully eliminate the remaining difficulties restricting performance, the following cost estimates in Table 7 should be valid. If the assumption seems unsound the reader may substitute the assumption of a well-engineered plant without reference to the Harleyville design. All basic cost figures are actual, as of March 1946 levels, and assumptions in addition to the one noted are made only in the projection to full rated capacity of the several factors such as coal consumption, power, fuel oil, and reagents.

TABLE 7—*Production Costs, Harleyville Plant Estimated for Full Capacity Production and Bulk Shipment of Alumina*
Cost Basis as of March, 1946

	Monthly Cost	Per Ton Calcined Alumina
Payroll, (including all salaries) \$37,600.		
Payroll taxes, 4 pct. 1,504.		
Compensation, 2 pct 752.		
	\$39,856	\$26.57
Coal, 3400 tons at \$6.40 21,760		14.51
Fuel oil, 45000 gal at 4.1¢ 1,845		1.23
Soda ash, 120 tons at \$30.60 3,672		2.45
Other reagents 3,000		2.00
Fire brick 2,800		1.87
Freight on clay, 7000 tons at 55¢ 3,850		2.57
Power, 1.15 million kw-hr at 5.3 mills 6,095		4.06
Spare parts and supplies 6,000		4.00
Office expense, legal and auditing, travel and miscellaneous 2,000		1.33
Production cost, exclusive of business taxes and amortization \$90,878		\$60.59

The labor cost at Harleyville was higher than it would otherwise be through design features which required excessive operating labor. Consolidation of buildings, elimination of expensive material handling, elec-

trification of pit pumping and other similar measures could reduce payroll costs by \$4500 per month and the cost per ton of alumina to \$57.00 per ton. In justice to the Architect Engineer it should be noted that most of these excessive costs were necessitated through wartime restrictions on plant design. In this tabulation no credit is allowed for by-products, a subject that will be discussed later.

It would not be feasible, for a number of reasons, to enlarge a plant at the Harleyville location beyond about 3 times its rated capacity. A series of estimates were made up, on a basis similar to that of Table 7, for larger capacity plants at a location where freight charges on clay might be reduced through proximity of clay and limestone deposits. The chief per ton cost reduction in larger plants, other than the freight item, is due to relative reduction in labor cost. The breakdown of these estimates is shown for one case in Table 8 below, and intermediate cases are illustrated in Fig 12.

TABLE 8—*Estimated Production Cost 500 Tons Alumina Per Day*

	Preferred Location, 500 Ton Capacity	
	Monthly Cost	Per Ton Calcined Alumina
Payroll	\$100,000	
Payroll taxes, 4 pct.	4,000	
Compensation	2,000	
Payroll, sub-total	106,000	
Coal at \$6.40 per ton	199,040	13.27
Fuel oil at 4.1¢ per gal	16,800	1.12
Soda ash at \$30.60 per ton	36,720	2.45
Other reagents	27,000	1.80
Fire brick	17,500	1.17
Freight on clay 55¢ per ton	14,000	0.93
Power at 5.3 mills per kw-hr	42,400	2.83
Spare parts and supplies	54,000	3.60
Office expense, legal and auditing	3,600	0.24
Travel and miscellaneous	5,000	0.33
Total cost exclusive of depreciation	\$522,060	\$34.81

In view of postwar conditions, capital cost estimates are difficult to assess except on the basis of actual cost of the Harleyville

plant, with some reduction on account of simplifications, particularly in the desilication section. A graphical illustration similar to that appearing in the earlier paper on

outlet to specialized markets can be foreseen for the tonnage of residue involved, at a price that should net \$5.00 per ton of residue at the plant, before preparation.

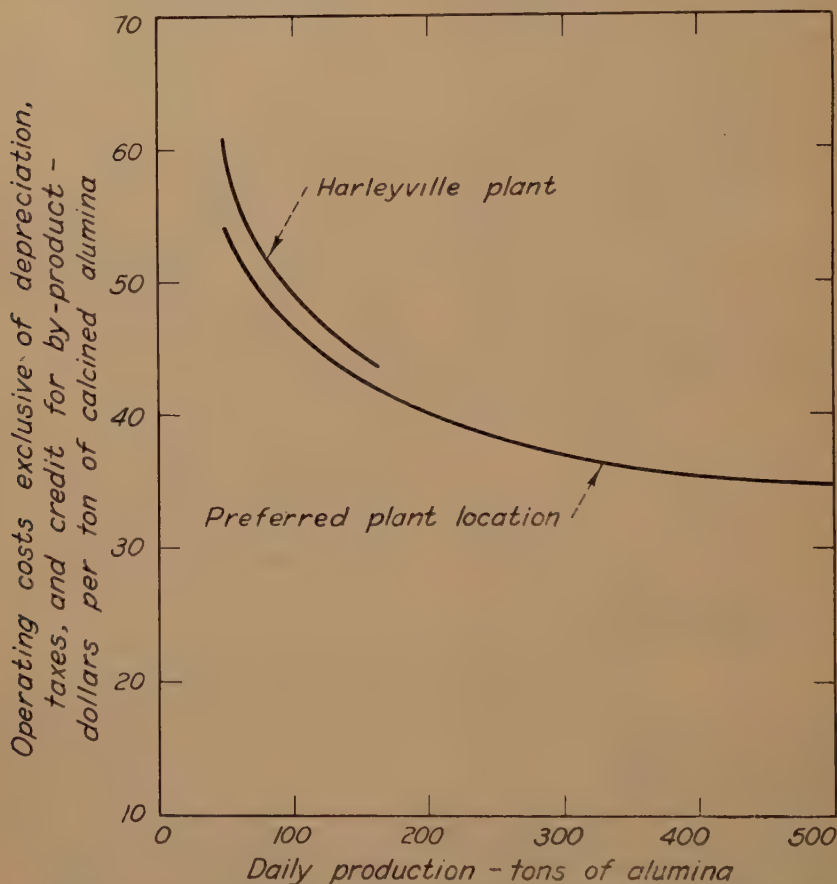


FIG 12—OPERATING COSTS VS. PLANT CAPACITY. ESTIMATED ON BASIS OF HARLEYVILLE EXPERIENCE.

Note: Usual amortization and interest charges would add approximately \$10 per ton to the production cost figures shown in Table 8 and Fig 12.

this subject is shown in Fig 13. The construction cost basis should be considered as of December 1944.

Since 7 to 7½ tons of residue are produced from the lime-sinter process for each ton of alumina, the possibilities for a market for this product enhance considerably the economic picture presented up to this point. For small plants, up to 100 tons of alumina per day, a possible

If this were applied as a credit against the cost of alumina production, the latter could be reduced by \$35.00 per ton from the totals given for small plants in Tables 7 and 8 and Fig 12. For plants of larger capacity, if it were desired to get maximum return by selling the entire output of residue, it would be necessary to exploit larger tonnage outlets, and the logical step would be to combine a Portland cement

plant with the alumina plant. For this use credit could not be expected to be over \$1.00 per ton of residue, or \$7.00 per ton of alumina.

equal to three tons of limestone in observable benefit to pastures, for example. The value of dicalcium silicate in rendering phosphate fertilizers more available to

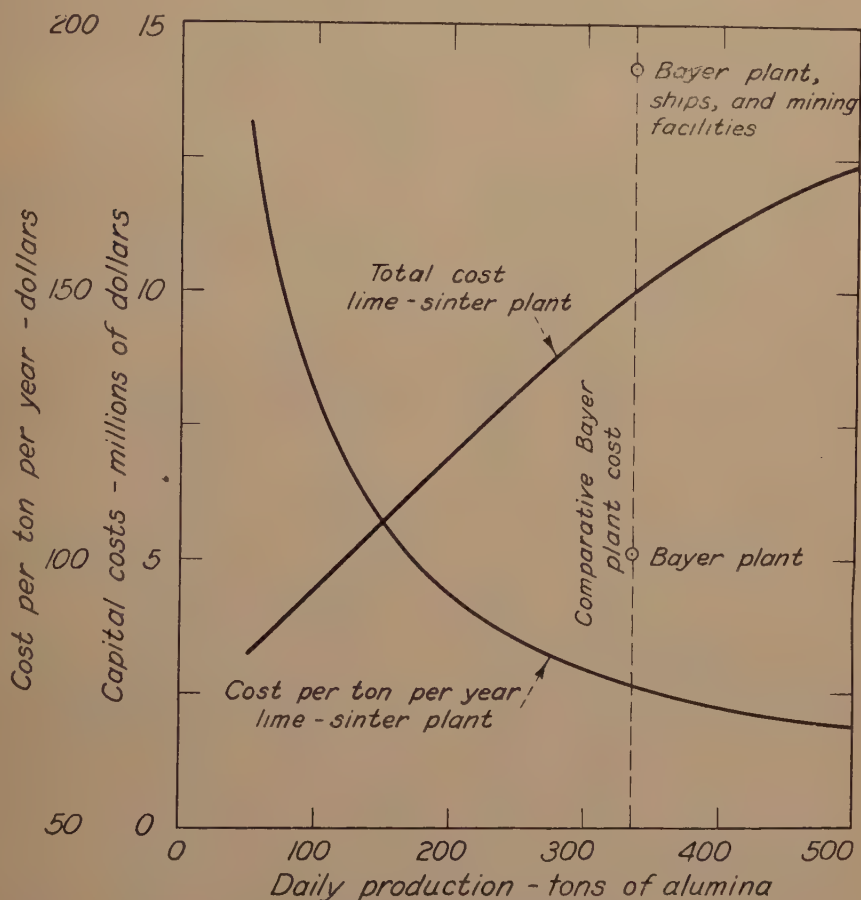


FIG 13—PLANT COST PER TON OF CAPACITY.

Estimated on basis of Harleyville experience for lime-sinter plants; and Engle, Gregory and Mosse's estimates for Bayer plants.

The estimated credits for by-products are based, in the case of Portland cement, on the result of pilot-plant trials, insofar as suitability of material is concerned; and on published information with respect to operating costs. The specialized markets to which reference has been made are found in: (1) agriculture, where one ton of dicalcium silicate residue has been shown

plants, or even substituting for phosphate, has been widely reported;⁶ (2) the plastic industry, where by actual trial it has proved to be a satisfactory mineral filler. Other industries employing mineral fillers have reported favorably on its value; (3) general industry, as a filter aid showing very desirable properties for clarification of certain solutions.

The chemical composition of residue from satisfactory treatment of clay and limestone according to the process described, is typically as follows:

	PER CENT
CaO.....	56.97
SiO ₂	24.00
Fe ₂ O ₃ + TiO ₂	1.83
Al ₂ O ₃	3.00
MgO.....	0.83
Na ₂ O.....	0.34
Minor constituents.....	0.45
Loss on ignition.....	12.58

As already noted, the particle size is largely in the range 2 to 10 microns. One sample from plant production showed, from sizing in a Haultain infrasizer, 98.2 pct minus 20 microns in particle size.

The statements relating to the value of the residue in agriculture are based on the results of work conducted on the Harleyville plant residue product at Clemson College and Experiment Stations in South Carolina. Those relating to other industries are based on the results of trial shipments and sales over the period of a year and reports from industry thereon.

ACKNOWLEDGMENT

It has been possible in this paper only to touch the salient points in the story of the alumina-from-clay project at Harleyville. It is based on a complete and detailed

report submitted to the Engineering Division of Reconstruction Finance Corporation, and acknowledgment is due this agency for permission to publish the paper. Acknowledgment is also made to the officials and staff of Ancor Corporation, particularly W. G. Hubler, President; and to E. O. McMahan, formerly Chief Chemist at the Harleyville Plant, who carried out the desilication studies.

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The Ammonium Sulphate Process for the Extraction of Alumina from Clay and Its Application in a Plant at Salem, Oregon

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(New York Meeting, February 1948)

THE problem of extracting alumina from clay and low-grade bauxites has been the subject of considerable interest for some time. The basic reason, of course, lies in the fact that known reserves of high-grade bauxite are not inexhaustible and that the present commercial process cannot successfully cope with low-grade bauxites or clay. Ultimately it may be necessary to use these poorer raw materials for all commercial operations.

An unprecedented demand for aluminum during the war emergency and the constantly threatened shortage of imported bauxite caused the United States Government to take an active role in this problem. Through the National Academy of Sciences, the War Production Board and the Defense Plant Corporation, it investigated processes and finally selected four to be used in the construction and operation of four experimental plants. Each plant was to be designed in such a way as to facilitate its incorporation into a larger commercial plant should the need arise. The Chemical Construction Corporation process, or "Chemico" ammonium sulphate process as it is better known, was one of the four selected.

The extensive literature and patents on record before the war generally follow one of two process-types depending upon the extracting reagent used. One group uses an acid reagent, the other an alkali. The

Chemico process uses an acid reagent. For those interested in other processes described in literature, there is a short bibliography at the end of this paper.

The basic steps of all acid extraction processes are: (1) to make the aluminum silicates acid soluble, (2) to separate the released alumina from impurities and insoluble gangue, and (3) to recover the reagent for re-use.

THE PROCESS AS PLANNED

In April 1941, a group of chemists and engineers of the Chemical Construction Corp. became interested in the problem of extracting alumina from clays and low-grade bauxites and, under the leadership of Mr. Blakeslee Barnes, Vice President and General Manager of the Company, first drafted a process in July of that year—five months prior to Pearl Harbor. The work continued in our research laboratories and with a small pilot plant. By June 1943, the work had progressed to a point where it was possible to apply for a patent on the process which was U.S. patent 2,405,426, granted August 6, 1946.

Immediately prior to the development of the Salem plant, the process was envisaged to be as follows:

1. The first step was to make the aluminum silicates acid soluble. It was planned:

(a) Clay or low-grade bauxite would be roasted at 700 to 800°C (1292° to 1472°F).

(b) The roasted ore would then be leached with hot aqueous ammonium bisulphate to form a slurry. In this way the

Manuscript received at the office of the Institute March 5, 1948. Issued as TP 2473 in METALS TECHNOLOGY, December 1948.

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alumina content of the clay would go into solution as aluminum sulphate. Some iron, titanium and practically all of the potassium and sodium would enter the solution as well.

2. There followed the step of separating the solubilized alumina from impurities and insoluble gangue:

(a) The slurry would be pumped to thickeners and the solution separated from the insoluble impurities which were to be washed and discarded.

(b) The solution would then be treated with ammonium bisulphite in order to reduce the iron salts to a ferrous state.

(c) The hot, nearly saturated solution would be cooled under controlled conditions so that the alumina content would crystallize out as ammonium alum, leaving the iron in solution.

(d) The crystals would be separated from the mother liquors by decantation and filtration and then washed on the filter.

(e) Once separated, the crystals would be redissolved and treated with aqua ammonia so that the alumina content would precipitate from it as aluminum hydrate. The sulphate radical would remain in the solution as ammonium sulphate.

(f) The aluminum hydrate would be filtered and washed from its mother liquor.

(g) It would then be calcined to an anhydrous nonhygroscopic material.

3. There remained the step of recovering the ammonium sulphate for re-use:

(a) The ammonium sulphate solutions from the aluminum hydrate precipitation step would be used countercurrently to wash the ammonium alum. They were to be later exposed to an oxidizing condition wherein the iron salts would be reconverted to the ferric state, ammonia added and ferric hydroxide precipitated in such a form as to make a dense, filterable hydrate.

(b) The ferric hydrate would be separated from the ammonium sulphate solution, washed and discarded.

(c) The ammonium sulphate solution would be concentrated and crystallized to be later processed to ammonium bisulphate and ammonia.

(d) The ammonia would be recovered as weak aqua, rectified and re-used in the precipitation of aluminum hydrate and ferric hydrate—thus completing the cycle.

When necessary, a portion of the mother liquors would be pumped from the system to be treated with lime and run through a still for the recovery of ammonia content. The solution of potassium, sodium and other sulphates would be discarded.

The use of ammonium bisulphate as the digesting agent presupposed a method of producing it on a practical and commercial scale. The engineering problems involved in accomplishing this step, such as heat transfer, temperature control, and even the acquisition of adequate construction materials, seemed to be insurmountable until a salt-bath type electric furnace was considered. The possibilities of this method of approach were thoroughly investigated and extensive experiments were conducted—some with units of a commercial size. By March 1943, it was definitely established that the resistance characteristics of the molten ammonium bisulphate to the passage of an electric current could be utilized and controlled in order to supply the heat necessary for the reaction. By adding a small amount of superheated steam there was no appreciable decomposition of the evolved ammonia gas and no other secondary reactions. The solution of this, the key problem, permitted the Chemical Construction Corp. to view the whole process as being a practical one.

It might be added that both engineers and chemists worked closely together at all times on this project. Our object was to develop and design a workable process in the shortest amount of time. For this reason the plans and specifications of a plant designed to produce approximately 50 tons of

alumina per day were well along when the research work was brought to a close.

proper equipment were hard to obtain and it was difficult to hold an adequate and well-trained labor force.

DESCRIPTION OF OPERATIONS

With the government's selection of the Chemico process as one of the four to be used in experimental plants, construction

Raw Material

When it came to procuring raw materials further difficulties were encountered, one

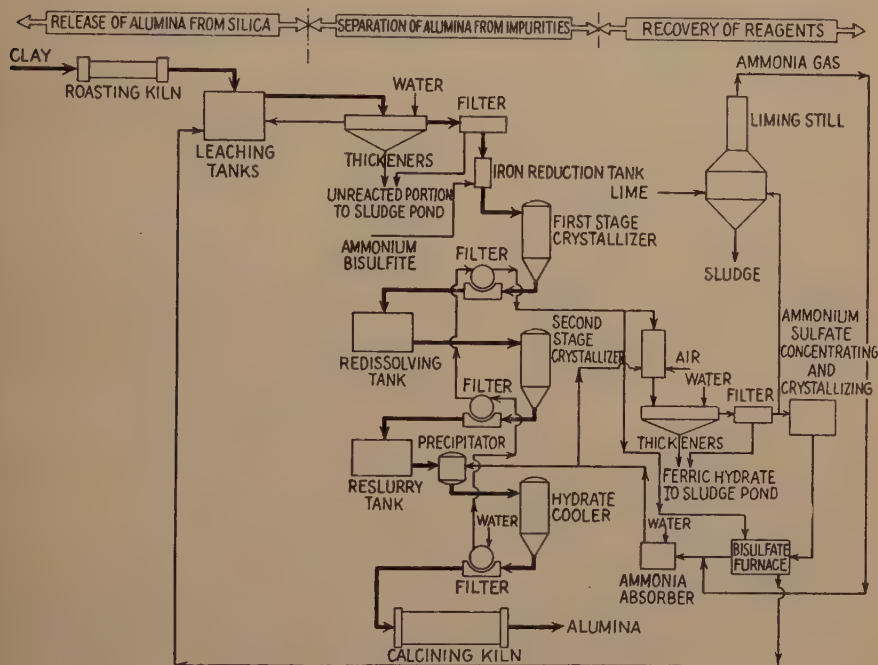


FIG 1—FLOWSHEET OF CHEMICO PROCESS.

of the plant was begun early in 1944. It was substantially completed at the end of 1945. Experimental operations were conducted in the six months period ending July 1, 1946, at which time the plant was shut down and turned over to the government at their request. Fig 1 is a flowsheet of the operations.

The plant site selected by the War Production Board was located at Salem, Oregon, and the land was acquired by the government through the Defense Plant Corporation. The construction and short operation of the Salem plant during war-time were hampered by the usual difficulties of the time. Construction materials and

of which clearly demonstrated the flexibility of our process. One of the reasons for locating this experimental plant near Salem was because of the enormous deposits of clay in that area. The original plan had been to use the Hobart Butte clay, a hard flinty product which was to be crushed to $\frac{1}{4}$ -in. size in a hammer-mill prior to roasting in a direct-fired rotary kiln. The units had been designed for that particular clay. Negotiations for the procurement of Hobart Butte clay failed, however, and it was necessary to use a substitute material, Cowlitz clay, found near Castle Rock, Wash. This clay varied greatly from the other in its physical

characteristics as well as in its analysis. It became soggy and then soupy during the rainy season of the Pacific Northwest. A hammer-mill might well have been exchanged for a sludge pump. The clay ran much higher in iron content and other impurities than did Hobart Butte and it also contained siderite or iron carbonate in the form of rocks ranging from the size of a baseball to that of a football. The fact that we were still able to produce exceptionally pure alumina from it is a most vivid demonstration of the flexibility of our process.

A composite sample of the Cowlitz clay shipments from Castle Rock analyzed as follows on a dry basis:

COMPOSITION	PER CENT
Loss of Ignition.....	16.60
Al ₂ O ₃	34.91
SiO ₂	38.28
Fe ₂ O ₃	5.85
TiO ₂	2.30
P ₂ O ₅	0.55
CaO.....	0.31
Undetermined.....	1.20

The above analysis does not include the siderite since as many of the rocks as possible were picked out by hand prior to delivery to the roasting unit.

The other difficulty that we encountered in procuring raw materials had to do with ammonium sulphate, the basic reagent in our process. This material was unobtainable when we needed it. Arrangements had to be made quickly to produce it at the plant from sulphuric acid and anhydrous ammonia.

The following is a general description of the equipment, processing and the results obtained at Salem. Before discussing them, however, it should be explained that the plant was never operated as a whole. This was because of the scarcity of labor and of our having to close down operations so soon after the plant was completed. In fact, all that we had time to do was the routine tuning up of each section of the plant. From that work, however, we gained valuable experience and more than ample proof of the process.

Clay Roasting

Reference has already been made to the type of clay finally used.

Fundamentally, the equipment consisted of a Williams hammer-mill; a brick-lined rotary kiln, 8 by 130 ft; a partially brick-lined cooler, 7 by 30 ft, with blowers; belt conveyors; dust collectors; and the usual adjuncts. The roasted clay was pulverized in a Raymond mill of 50 tons per hour capacity to approximately 50 pct through 100 mesh. It was stored in a concrete silo 24 ft in diameter by 36 in. high. Empirical laboratory tests on Cowlitz clay indicated that 85 to 90 pct of the alumina content could be extracted later if the clay were roasted at a temperature of approximately 750°C (1382°F). This figure was never actually obtained although the product did improve steadily as the operators' knowledge and experience increased.

The only important technical difficulty that we encountered concerned particle size, which varied widely at the discharge end of the kiln. The clay would tend to "ball up" at the feed end of the kiln because of excessive moisture and would never break down properly. At a given temperature the extremely fine material would be overburned, while the interior of the coarser particles would be underburned. It was found that the drier the clay feed, the less the trouble. It is felt that a predrier will be necessary for clays exceeding 15 to 20 pct in free moisture.

Clay Leaching

This unit consisted of four round steel tanks, lead and brick-lined, and connected in series with the slurry flowing from one to another by overflow pipes near the top of the tanks. The tanks are 18½ ft id by 10½ ft high and had a capacity of 21,000 gal each. Each tank was agitated with a Durimet turbine-type agitator.

Molten ammonium bisulphate from the electric furnaces was run directly into the

first digester, together with roasted clay and wash solution from the sand washers or direct water. The reaction was strongly exothermic and much of the water was evaporated at this point. The alumina in the clay went into solution in the form of sulphate together with sodium, potassium, magnesium and other alkali or alkaline earth elements present in the clay. The same was true of iron but not to the same extent. By maintaining proper roasting conditions, which vary with different clays, maximum solubilization of the alumina content could be realized with only partial solubilization of the iron. The initial clay-roasting step was, therefore, of paramount importance to the process as a whole.

This unit was never operated at a rate of more than 25 pct capacity. Only one out of the four electric furnaces supplying the molten bisulphate was operated at a time. An average of approximately 85 pct of the solubilized alumina in the clay was recovered in the solutions. A greater percentage of alumina was extracted than was anticipated by the laboratory tests since a greater proportion of ammonium bisulphate was used in the plant.

While routine operating conditions were never attained, no major changes were indicated. The equipment was designed to handle 230 tons of clay per day and 450 tons of ammonium bisulphate. It is believed that that rate can be easily achieved with the production of a uniform, nearly saturated solution capable of efficient extraction.

The temperature of the digestors was approximately 166°C (233°F), the boiling point of the slurry. The alumina content of the solutions going to the sand washers was $4\frac{1}{2}$ pct, corresponding to a 90 pct saturation at 80°C (176°F).

Sand-washer Thickeners

The slurry from the digestors was pumped through a Durimet pump to the thickeners where the hot, nearly saturated

solution was separated from the insoluble ingredients. These were then washed countercurrently with water and discarded. The wash water from No. 3 sand washer was pumped to the digesting unit, already discussed.

The unit consisted of 6 thickeners, 60 ft in diameter, 10 ft high, and of 250,000 gal capacity each. They were of concrete construction, lead and brick-lined. The rakes of the first two units, which were operated in parallel, were covered with lead while the remaining four were covered with neoprene. The plows of all the rakes were Durimet. Rubber-lined, underflow and overflow pumps were provided. The sand washers were batch operated rather than continuously as designed. This was because of the stepwise operation of the plant which had to be used. Their storage capacity proved to be very useful for this type of operation.

Under the conditions outlined no exact data could be given regarding the capacity or efficiency of the equipment. It is felt that the substitution of a vacuum filter after the third sand washer in place of the last three sand washers might be desirable. It would certainly lower the capital investment. It is also thought that a clarifying filter might be necessary for the pregnant solutions on being discharged into the liquor tanks. In addition, there is some question as to whether the solutions would be free of all insoluble sediment if the unit were operated at rated capacity.

Iron Reduction

The overflow from the sand washers ran into a storage tank, lead and brick-lined and having a capacity of about 50,000 gal, from which it was pumped to the iron reduction equipment. This unit consisted primarily of a Glens Falls sulphur burner and absorption tower where aqua ammonia and sulphur dioxide gas were brought together to form an ammonium sulphite-bisulphite solution of a strength equivalent

to 20 to 25 pct sulphur dioxide content. This solution was pumped to the reduction tank under controlled conditions where the iron salts of the hot solutions from the sand washers were instantly and completely reduced to the ferrous state. An excess of reagent corresponding to 0.01 to 0.02 pct sulphur dioxide was maintained in the treated solution to prevent subsequent reoxidation.

The reduction tank was of steel, 4 ft in diameter by 10 ft high, lead and brick-lined, and supplied with a Durimet agitator. The tank was built for pressure and the operation was carried on at about 50 lb pressure.

There were no difficulties encountered with this unit and there was no doubt as to its being capable of operating at designed capacity.

Alum Crystallization

In this operation, the hot pregnant solution was subjected to controlled cooling. Nearly all the alumina content was crystallized out in the form of ammonium alum in a very pure state except for the alkali and alkaline earth metals which crystallize out isomorphously. Small amounts of suspended particles carried over may also be occluded in the crystals and interfere with the crystal growth. The iron remained in the mother liquor, however, together with any excess of ammonium sulphate over that required to form the alum. The alum crystals consisted of one mol each of aluminum sulphate and ammonium sulphate plus 24 mols of water. The alumina content corresponded to a little over 11 pct.

Two primary requisites of the operation were: (1) cooling to a sufficiently low temperature, and (2) the formation of proper size crystals—too small to occlude any appreciable amount of ferrous sulphate but large enough to be filtered or classified with ease from the mother liquor. The solubility of alum in 20 pct ammonium sulphate solution, for instance, was 1.7 pct at 25°C

(77°F) which corresponded to around a 90 pct recovery of the alumina content. To indicate the magnitude of the iron removal obtained in the final product, about 1999 parts of iron oxide out of every 2000 in the hot pregnant solution were removed.

The equipment as designed and installed called for 2 crystallizations and consisted primarily of 2 vacuum crystallizers operating in series with each discharging crystal slurry into separate rake-type classifiers. The crystallizers were steel, rubber-lined tanks 8 ft in diameter by 15 ft high supplied with circulating pumps to control crystal growth. The classifiers were also rubber-covered throughout. The unit was designed to operate continuously but did not function as planned. It proved impossible to obtain a low enough temperature to get the degree of alum crystallization desired. In addition the crystal size first obtained was too small for processing by any known means. It was found that a part of this was caused by the solution being subjected to "shock cooling" when pumped into the crystallizer. This caused the alum to precipitate or "salt" out in the form of extremely small crystals rather than enter the solution and then crystallize out. It was found necessary to operate the crystallizers batchwise which resulted in quite uniform crystal sizes, considerably larger than those previously attained.

In summary, it was found that the crystallizers had been underdesigned both as to minimum temperature required and as to capacity whether run continuously or batchwise. It was also found that the classifiers were entirely incapable of handling the slurry supplied. It soon became evident that some other type of equipment would have to be furnished to produce the desired results.

Alum Filtration

Salt-type filters had been originally designated for processing the slurry received from the alum crystallizers. The

idea was abandoned, however, because it was believed, at that time, that there would be difficulty in washing the crystals on them. Since the rake-type classifiers had been proved inadequate for separating the crystals from the mother liquor, we were finally forced to resort to vacuum-type filters.

Three vacuum drum filters, 8 ft in diameter by 12 ft, face had been installed to filter the aluminum hydrate further down the process and arrangements were hastily made to use them as substitutes. The crystallizers and filters were installed rather far apart and a considerable amount of time was lost in adding the necessary piping and other connections.

The "flow" was now as follows: The original solution was crystallized batchwise in the first crystallizer, the slurry pumped to No. 1 filter, where it was filtered and washed. The crystals were then redissolved in hot ammonium sulphate solution, recrystallized in the second crystallizer and filtered and washed on No. 2 filter, then transferred to the aluminum hydrate precipitation step. Because of the presence of a very small amount of a gelatinous substance which blinded the filter cloth, it was necessary to decant the cloudy solution from the settled magma before filtering.

While the crystals were always finer than desired the operation soon proceeded very smoothly. To make an easily filterable and washable cake it was found that rather close limits as regards pH and density of the slurry had to be maintained. Once the proper conditions had been established, a thick, uniform cake was formed which would take all the wash that could be applied. It was determined that the step was entirely practical for the production of nearly iron-free alumina at this point.

Alumina Precipitation and Filtration

The Chemico process as designed next called for redissolving the crystallized alum

as a hot concentrated solution. It was then to be treated with a 50 pct aqua ammonia solution so as to precipitate the alumina as aluminum hydrate, leaving the sulphate radical in solution as ammonium sulphate.

For this purpose, 8 vertical cylindrical tanks were installed each 11 ft in diameter by 8 ft high, lead and brick-lined, and capable of withstanding a maximum pressure of 50 lb. Each unit was supplied with a turbine-type agitator and steam coils. The flow of each ingredient was controlled closely with pH equipment. Our main object in this step was to produce a dense aluminum hydrate precipitate of reasonably large agglomerates so that it could be filtered and washed easily prior to calcination.

In our original experiments, it had been shown that the precipitate could be partially dehydrated if the temperature were elevated. This had resulted in a denser precipitate, thus facilitating filtration and reducing the fuel requirements in the subsequent calcination operation. Steam coils capable of elevating the temperature to 130°C (266°F) had been incorporated in the units for this reason. The work at Salem confirmed the results of the earlier experiments. Elevated temperatures definitely aided the formation of a more filterable precipitate. Despite our original experiments, however, changes were found to be necessary both in the process itself and in the equipment handling it.

In the revised process a predetermined amount of 6 pct aqua ammonia was pumped into the precipitator tank followed by a predetermined amount of washed crystal slurry direct from the alum filter. The equipment was changed because the turbine-type agitators installed had proved to be entirely unsatisfactory. They broke up the precipitate agglomerates in the immediate area and failed to mix the contents of the whole vessel. The product was slimy and unfilterable. A sweep-type agitator was substituted and resulted in a gentler and

more uniform agitation. With these changes, we were able to produce a satisfactory precipitate in which the agglomerate structure was preserved to the fullest degree.

Calcination

The central piece of equipment was a rotary kiln $10\frac{1}{2}$ ft in diameter by 185 ft long, lined with 6-in. brick and equipped to burn fuel oil countercurrently to the flow of material.

The aluminum hydrate was fed into the kiln by means of a variable screw feeder from an overhead bin. The calcined material was discharged into a cooler and then to the storage silo by means of an air conveyor system. The exhaust gases were first drawn through cyclone separators and then to a spray tower to remove the extremely fine dust which was ultimately pumped back to the filters. The calcining temperature was maintained at approximately 1150°C (2102°F). The unit was not operated long enough to warrant any firm statements as to its capacity or performance. However, no operating difficulties were encountered. The indications were that the particle size might be coarser than specified by reduction plants.

The calcined product did not approach the quality of the feed before the plant was permanently shut down. This was undoubtedly caused by the fact that it takes a long time to purge all foreign matter from a new calciner.

Iron Oxidation and Mud Washing

Condensate, or as pure a water as obtainable, was used as wash on the last hydrate filter and the resulting solution processed countercurrently through the aluminum hydrate and the alum filtration steps. It was then mixed with the mother liquor from the first alum crystallization to be reprocessed for recovery of ammonium sulphate.

The first step was to remove the iron and

the alumina remaining in the solution. To do this, the iron had to be oxidized back to the ferric state, ammonia added to a pH of 8 to 8.3 whereby ferric hydrate and alumina hydrate were precipitated and then either filtered or settled out to be washed and discarded later.

The basic equipment consisted of a round wooden tower $4\frac{1}{2}$ ft in diameter by $51\frac{1}{2}$ ft high filled with wooden grill work over which the mother liquor was to be pumped. Ammonia in the form of 15 pct aqua was introduced through the sides of the tank at proper levels and air was drawn up through the length of the tower by means of a blower with the idea of simultaneously oxidizing and precipitating the hydroxides. The muddy solution would then flow into a master thickener 60 ft in diameter, lead and brick-lined. The underflow was to be pumped countercurrently through a series of 5 small thickeners 20 ft in diameter. The washed solids were to be pumped to waste. The clear or nearly clear overflow from the master thickener would pass into a mixing tank where filter aid would be added when necessary. It was then to be pumped to the ammonium sulphate crystallizer through continuous pressure type filters. The equipment was never operated as designed because of the irregular operations in the primary phase of the process.

Our experiments prior to the Salem operations had established the conditions necessary to bring about a dense, rapid settling hydrate. These conditions were never duplicated at Salem and, as a result, the solids never settled out as had been hoped.

In order to accelerate the operation and accumulate mother liquors quickly, it was decided to experiment with one of the then idle digesting tanks. A lead spider for introducing compressed air and another for ammonia were installed in it. Use was made of the very thorough mechanical agitation

available. The development proved to be highly successful; oxidation was complete within a matter of minutes. It is probable that this method will be adopted in the future to replace the packed tower.

The hydrate still did not settle as desired, however, and it was decided to experiment with filtering the precipitate on the vacuum filters. The results exceeded all expectations. It is believed that with further development work, vacuum filtration will be quite practical for this step.

Ammonium Sulphate Crystallization

The clarified solution from the iron oxidation was to be evaporated and the ammonium sulphate content crystallized out, centrifuged and transferred to the ammonium bisulphate department.

The equipment was a "Krystal" or "Oslo" installation, comprising two duplicate units in double effect and consisting essentially of evaporators, crystallizers (rubber-lined) heaters and circulating pumps. The resulting crystal slurry was pumped to a battery of 9 Sharples continuous centrifuges from which the crystals were discharged with 3 to 5 pct water content. The entire unit was designed to produce approximately 535 tons of crystals per day on the basis of a 46 pct solution. It was the largest installation of its kind ever built and included features different from conventional design.

The development of an operating technique for this equipment was a major task in itself. Changes had to be made and much trouble resulted from porous pump casings. The most serious trouble developed with the rubber linings which soon began to fail. They finally had to be completely replaced with stainless steel. A great many of the difficulties that were encountered in this step were caused by materials of construction that had to be used as substitutes for those we preferred but which were unobtainable when the plant was built.

The production of crystals from a solution of ammonium sulphate is a rather simple and well known process which need not be described further.

The rated capacity of the unit was never attained. It is probable that additional equipment would be required to avoid excessive losses through foaming and other factors.

It has already been mentioned that ammonium sulphate had to be produced at the plant because of our inability to purchase it elsewhere. The crystallizer was used for this purpose and it was operated at a rate in excess of our own requirements. The surplus product was diverted to agricultural needs in the area. This arrangement made possible the planning of a definite development and production program since our own needs were so small and irregular.

Ammonium Bisulphate Production

The equipment consisted primarily of 4 covered 3-phase electric furnaces. The furnace shells were round with 12 ft id and 7 ft deep, lined with sil-o-cel and Duro brick. The energy was supplied through three 20-in. graphite electrodes at voltages which could be varied from 123 to 163 v. The transformers had a capacity of 3125 kva each. Superheated steam was introduced into each furnace through 6 Duriron pipes with nozzles at the ends to circulate the molten bath and retard secondary reactions. The superheated steam was supplied by two oil-fired superheaters capable of delivering 8000 lb per hr at 400°C (752°F) each.

The mixture of steam and ammonia gas from each furnace was drawn through scrubbing towers 6½ ft in diameter by 22 ft high over which was circulated a hot ammonium sulphate solution to dissolve any dust or sublimed ammonium sulphate, and then delivered to the ammonia recovery system.

The furnaces were kept at a slight

vacuum by means of automatically controlled valves. The optimum temperature for this operation was found to be 380 to 390°C (716 to 734°F) and the molten product, which was run directly into the clay digestors through brick-lined troughs, analyzed 85 pct ammonium bisulphate and 15 pct ammonium sulphate. This could very likely be improved with more experience in operation. Only one furnace was operated at a time. The desired temperature could easily be maintained by controlling the feed of ammonium sulphate.

The actual power consumption was 350 kw-hr per ton of ammonium sulphate charged as compared with the theoretical figure of 330 kw-hr. This corresponds to a power consumption of around 3500 kw-hr per ton of alumina produced, assuming a circulating load of 10 tons of ammonium sulphate per ton of product.

Superheated steam at a temperature corresponding to that of the bath was blown in at a rate corresponding to about 0.2 lb steam per pound of ammonium sulphate feed.

The operation proceeded smoothly from the very beginning and, as indicated by the power consumption, secondary reactions, such as the formation of pyro sulphate or gaseous oxides of sulphur were negligible. Time did not allow a thorough investigation of the extent of ammonia decomposition to elemental nitrogen but the tests that were made indicated this to be of very low order of magnitude. However, the retarding action of the steam was necessary.

Ammonium Recovery and Rectification

The mixture of steam and ammonia gas, with some air as the result of leakage around the covers of the bisulphate furnaces under the slight vacuum maintained, was first drawn through the scrubbers. At this point much of the steam was to be condensed and the sublimed ammonium sulphate and dust scrubbed out. It was then

to be passed through the exhaust fan and into the ammonia recovery system.

The basic equipment consisted of two "coke boxes" connected in parallel each 20 ft in diameter and 15 ft high and partially filled with coke, a tubular condenser, a blower and an absorber. Water was recirculated over the coke boxes to eliminate any trace of sublimed solids and to condense more steam. A part of the solution was continuously transferred to the scrubbing towers where it was pumped to the crystallizer for recovery of ammonium sulphate content. The equipment was designed to recover the ammonia as a 15 pct aqua. Air infiltration in the starting up period resulted in the recovery of a much weaker aqua. This weaker product nevertheless was used in order to reduce ammonia losses to a minimum.

The aqua was then pumped to the rectifier where it was absorbed in condensate at any strength desired up to 60 pct aqua. The unit was of standard manufacture consisting of a bubble cap tower, heat exchanger and so forth.

Liming

As the mother liquors build up in alkali and alkaline earth content, a portion must be periodically purged. The quantity to be purged is determined by the specifications of the final product desired and the analysis of the clay used.

The equipment was never used at Salem because of the short length of time that we operated the plant. It consisted of tanks equipped with agitators for mixing lime with the liquors and a still for stripping the ammonia from the mixture. The recovered ammonia was then to be returned to the system.

Auxiliaries

Brief mention must be made of two major auxiliaries, steam and water, because they are vital to the process and because

their development presented problems as formidable as the basic process itself.

The electric steam boiler installation was the result of a decision made by the Fuel Administrator. One 3-phase boiler was installed instead of 3 single-phase ones, as recommended by the vendor, because of a War Production Board order. As a result there was erected at Salem an electric boiler of 50,000 kva capacity consisting of a single shell with 3 iron electrodes. This was many times larger than any unit of its type built before. It was designed for a steam capacity of 150,000 lb per hour and 160 lb pressure.

The design called for the use of untreated river water filtered through screen filters to remove solid particles and a constant bleed of such proportions as to maintain constant resistivity. This was discharged through a pressure reducing valve into a deaerating tank and its heat energy transmitted to the incoming feedwater. Learning how to operate this boiler, particularly the starting up and shutting down steps, was a serious matter. Numerous unscheduled shut downs took place, some of long duration. These problems directly affected the planning of operation for the rest of the plant.

One major trouble was the feedwater. It was found that the quantity and quality of the silt in the Willamette River, from which the process water was pumped, varied widely with the seasons. Debris from a sulphite paper mill a few miles upstream contributed to this. The worst feature was a form of algae which appeared at various times. The combination made the screen filters wholly inoperable because of the formation of an impervious coating on the screen which could not be dislodged by any degree of backwash, and raw unfiltered water had to be used directly. The result was excessive scaling in the boiler even at the maximum rate of bleed. Even with filtered water available there was evidence that better circulation within the boiler would be necessary and provisions

were being made to improve this when the plant was shut down.

SUMMARY

A thorough examination of the results obtained at Salem clearly show that here is a workable process for the production of alumina from clay and bauxite. Mention has already been made as to the demonstrated flexibility of the process even when designed for a particular type of clay. The chemistry of the process is sound and the application of it appears to produce an alumina of very high purity.

An analysis of the aluminum hydrate produced and ready for calcination showed only the following impurities:

IMPURITIES	PER CENT
Loss of ignition.....	0.67
Fe ₂ O ₃	0.004
SiO ₂	0.012
TiO ₂	None
Na ₂ O.....	0.0001
K ₂ O.....	None
SO ₃	0.083

This compares extremely well with the specifications required by reduction plants.

As a peace time process, Chemico offers maximum flexibility as far as location is concerned. Access to a large deposit of suitable clay or bauxite is, of course, necessary, as it is for reagent chemicals. The only other factors to be considered are the usual: sources of fuel, power, labor and water, as well as proximity to markets. Advantage might be taken of certain other factors in particular instances. The use of bauxite, for example, would eliminate the preroasting step and simplify the digesting and sand washing steps thus reducing the plant investment. In areas of heavy demand for sulphate of ammonia for fertilizer purposes, the crystallizer could be so designed as to allow the separate removal of the first crystallizer product. The product value would be enhanced by its content of alkali and alkaline earth metals present in the mother liquor. Such a move would automatically eliminate the necessity of a liming tower.

In conclusion let us remember that the

Salem plant was authorized and erected to determine the potentialities of the Chemico process for the production of quality alumina from clay. From the experience gained, it is the opinion of the Chemical Construction Corp. that its process is a workable one capable of producing high purity alumina from almost any clay or bauxite with few, if any, limitations as to chemical analysis or physical conditions of the raw material. The process may well be an important one in the future for peace time production as well as in a national emergency.

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Production of Magnesium at Painesville, Ohio

By J. M. AVERY,* MEMBER A.I.M.E., AND R. F. EVANS†

MUCH has been written of the glamour of magnesium from sea water, the Aladdin-like creation of a huge magnesium plant in the Nevada desert using cheap hydro-electric power from Boulder Dam; the marvels of the Hansgird process for the electrothermal reduction of magnesium oxide by carbon, and the ferrosilicon process for producing magnesium from dolomite. This is the story of the production of magnesium by the electrolytic process, using steam-electric power supplied by a public utility, in a plant at Painesville, Ohio, 30 miles east of Cleveland on the shore of Lake Erie. The story is not without interest, since it involves several unique developments that provide the answer to a question frequently asked: How is it possible to produce magnesium metal economically at such a location as Painesville, Ohio?

Basically, the answer lies in making use of facilities already in existence for the production of soda ash, which makes it possible to manufacture magnesium chloride, the principal raw material, cheaply enough to offset the high cost of electric power. To this is coupled the successful conversion of by-product chlorine into a product required for the war program.

The source of magnesium for this opera-

tion is the enormous surface deposit of high-grade dolomite in the region south of Toledo, within reasonable freight haul of Painesville. This same geological stratum underlies the Painesville plant, but unfortunately at a depth of about 3000 ft.—apparently too great a depth to permit underground mining to compete with the delivered cost of rock from surface quarries in other areas. The cost of dolomite obviously is an important factor, since the rock contains only some 12 per cent magnesium (20 per cent MgO) so that one dollar on the cost of stone means more than \$8 in terms of its magnesium content, and more than that in terms of recoverable magnesium metal.

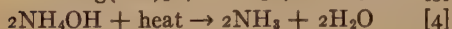
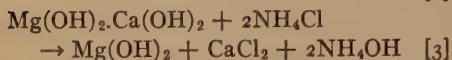
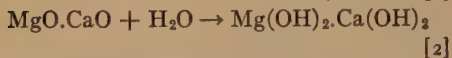
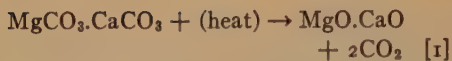
PRODUCTION OF MAGNESIA FROM DOLOMITE

In the summer of 1941, the Diamond Alkali Co. was well along with construction of a plant intended for the commercial production of refractory and other grades of magnesia from dolomite. The process to be used was designed to make maximum economic advantage of existing plant and operations by tying the production of magnesia in with the manufacture of soda ash in such a way as to make use of the lime (CaO) value of calcined dolomite. The process finally adopted after a lengthy research and development program has much in common with the old Clerc-Nihoul process, but includes certain innovations found to be necessary or advantageous. Essentially, the process is based upon the following series of reactions:

A description of a wartime development by Diamond Alkali Co. and its subsidiary Diamond Magnesium Co. Manuscript received at the office of the Institute Nov. 2, 1944. Issued as TP 1829 in METALS TECHNOLOGY April 1945.

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†Vice President and General Manager, Diamond Alkali Company.



Reaction 1 represents the calcining of dolomite to dolomitic lime. At Painesville this is done in vertical mixed-feed kilns (Fig. 1), in order to obtain high-strength

of hydrated lime ($\text{Ca}(\text{OH})_2$) with NH_4Cl to displace ammonia and generate CaCl_2 , while the $\text{Mg}(\text{OH})_2$ remains substantially unaffected. This reaction is carried out in the ammonia stills of the ammonia-soda process, and in so doing the lime content of the dolomite is used to replace ordinary lime. This provides a credit against the process and is one of the reasons for its economic success.

Reaction 4 represents in effect the completion of reaction 3 by the usual procedure



FIG. 1.—VERTICAL LIME KILNS, IN WHICH DOLOMITIC LIME IS PRODUCED.

tail gas (about 40 per cent CO_2) for use in the ammonia-soda process. As will be seen later, this tail gas is also directly useful in the production of magnesium chloride. The fuel used is coke from our own by-product coke plant at Painesville.

Reaction 2 represents the hydration of dolomitic lime under carefully controlled conditions to yield a product having the best physical and chemical properties for the ensuing operation.

Reaction 3 represents selective reaction

of steam distillation of the reaction liquor to remove ammonia, which is returned to the ammonia-soda process.

The residue from reactions 3 and 4, known as the blowoff liquor of the ammonia stills, is essentially a slurry of $\text{Mg}(\text{OH})_2$ in a solution of calcium chloride (CaCl_2) containing a substantial fraction of unreacted salt (NaCl) from the ammonia-soda process. For the production of magnesia, the next step is to separate the $\text{Mg}(\text{OH})_2$ by thickening and filtering, producing a

filter cake for further processing to the desired type of refractory or other magnesia product.

INITIATION OF GOVERNMENT PROJECT

By the time Diamond's magnesia plant based on this process was nearing completion, pilot-plant study of the production of magnesium chloride from this same blowoff liquor was also nearly finished. In the summer of 1941, the United States was deeply committed to supplying "non-shooting" aid to our future Allies, and it required no great stretch of imagination to guess that we would shortly be in a "shooting" war ourselves. At that time one of the most obvious critical shortages of war materials was magnesium metal, and frantic efforts were being made by the predecessor of the War Production Board to find ways and means of increasing capacity for its production.

Information regarding Diamond's interest in this field reached Washington, and we, along with others, were asked to undertake a magnesium-metal project in behalf of the Government. At that time the Cleveland area, including Painesville, was one of the few industrial areas of the country that offered the possibility of large blocks of surplus electric-power capacity, the labor supply was adequate, and substantial use of existing facilities and services made possible a project of which the capital cost would be low. All that was needed was selection of a process for making magnesium, with the Diamond Alkali Co. in the position of being able to use either dolomitic lime, magnesia, or magnesium chloride as raw material.

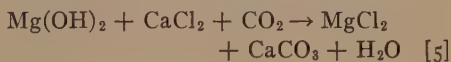
After carefully weighing the merits and drawbacks of known processes based on these different raw materials, decision was taken to adopt the Dow electrolytic process based on magnesium chloride produced in our own plant by our own process. Necessary arrangements with Dow were completed by the Government, and in October

1941 a contract was signed for us to build and operate in behalf of the Government a magnesium plant having a rated capacity of 36,000,000 lb. of metal a year. A subsidiary, Diamond Magnesium Co., was organized for this purpose.

This decision involved on our part the sacrifice of postponing the production of magnesia in our nearly completed plant, since the scale of operation required that all available capacity for magnesium oxide be diverted to the production of the chloride. However, in the interest of aiding the war effort, the Diamond Company gladly accepted the sacrifice, and ground was broken for the new plant in December 1941.

PRODUCTION OF MAGNESIUM CHLORIDE

Meanwhile, completion of pilot-plant work on the magnesium chloride project was rushed, coincident with design of a commercial plant. The process finally adopted was based upon carbonation of the slurry made up of magnesium hydroxide and calcium chloride, previously described, according to the simple reaction



This reaction is well known, and can be carried out in such equipment as carbonating towers or turbomixers, the former method being adopted by the Diamond Company. In this step, slurry from reactions 3 and 4 is used as is, after proper proportioning and preparation in settling tanks, the carbon dioxide required being obtained from reaction 1, i.e., the rich tail gas of the vertical lime kilns.

An interesting and economically important feature of this process is that the chlorine content of the magnesium chloride is obtained from cheap by-product calcium chloride liquor from the ammonia-soda process. In most other plants producing electrolytic magnesium, this chlorine is derived from the by-product magnesium-cell gas, either through conversion to

hydrochloric acid followed by wet reaction with dolomite or magnesia, or by dry chlorination in the presence of carbon at high temperature. In either case, make-up chlorine from electrolytic cells is required. Chlorine was at that time, and has since remained, one of the "critical shortage" chemicals for war purposes, and this avoidance of a need for make-up chlorine was therefore a matter of real importance in connection with our project. It was also our hope, and that of Government authorities, that we might somehow devise a method for helping out the chlorine situation by making use of the by-product cell gas for the production of chemicals needed in the war effort. As will be seen, this was successfully accomplished.

Reverting to the production of magnesium chloride, further processing after carbonation involves thickening and filtering to remove precipitated calcium carbonate, leaving a solution containing about 10 per cent $MgCl_2$ and some salt ($NaCl$). This solution is then evaporated to about 35 per cent strength for delivery to the magnesium plant, in the course of which most of the salt is precipitated and removed. After certain purification treatment, the solution is ready for conversion to cell feed.

This evaporation step, simple as it sounds, presented great practical difficulties. The solution is highly corrosive, and an extensive research program was necessary in order to find a satisfactory material for tubes and other evaporator parts. This problem was finally solved by the use of Inconel tubes. There are also certain side reactions possible, which can and do cause trouble in the evaporators unless suitable controls are exercised. However, these problems were all worked out satisfactorily, though not without tribulation, and the plant was ready to produce a satisfactory grade of chloride in time for the starting up of the magnesium plant.

This occurred in September 1942, nine months after ground was broken, and

successful operation has been maintained continuously ever since. The Dow magnesium process has been described elsewhere so fully and effectively that it seems unnecessary to burden our readers with that part of the Painesville operation. We therefore pass on to the problem of using the by-product cell gas for war purposes.

USE OF BY-PRODUCT CELL GAS

In the Dow process about 40 per cent of the chlorine evolved leaves the cells as HCl , the gases are heavily diluted with air, and considerable carbon dioxide is present. As far as we are aware, no use had previously been made of this gas other than to convert all of its chlorine content to dilute impure hydrochloric acid of low value, for which in our case no adequate market could be found. The problem then was to find some way of converting into a product useful in the war program, the free chlorine contained in the cell gases, amounting to 70 or 80 tons per day. This is equivalent to the capacity of a large electrolytic chlorine plant.

Studies based on this cell gas quickly indicated that it was unsuitable for dry chlorination or for most familiar chemical purposes. However, our studies were given both impetus and direction by a request from the War Production Board that if possible this chlorine should be converted into hypochlorite for decontamination of poison gas and general sanitation purposes. This was presented as an urgent requirement of the armed services, and the advantages of using otherwise waste chlorine were obvious because of the persistent critical shortage of chlorine. The economic advantage of the use of low-value chlorine was also an important consideration.

The difficulties were all too apparent, for it was necessary first to cool huge volumes of dilute cell gas, remove hydrochloric acid already present in the gas, and then somehow convert its remaining free chlorine content into hypochlorite in spite

of the presence of considerable carbon dioxide, known to be a deterrent to efficient conversion to hypochlorite. These

we believe this is its first application in the field of chemical absorption, where, judging from our results, it has a promising future.



FIG. 2.—SPRAY DRIERS, WITH TAIL-GAS SCRUBBER.

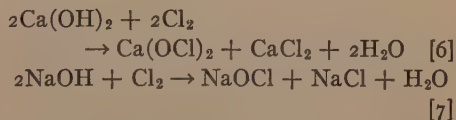
difficulties were magnified by the fact that the gas, containing only about 3.5 per cent chlorine by volume, was actually so lean as to be classed properly as a tail gas rather than a raw material. It was, moreover, important to produce not just "hypochlorite," but a high-strength, stable, solid product at a reasonable cost and with minimum requirement of critical materials and equipment.

It was found that the gas could be cooled and stripped of HCl by counter-current contact with cooled water in scrubbing towers already in existence. Research indicated that the chlorine could be absorbed from the stripped cool gas, without much adverse effect from carbon dioxide, by the use of special absorption towers of the Pease-Anthony type (Fig. 2). This type of scrubber was designed for the removal of dust from gases and has been used commercially for that purpose, but

A pilot-plant scrubber demonstrated that both caustic soda and lime slurry could be used in such absorption units to produce hypochlorite solutions efficiently and economically, with very low chlorine content in the tail gas. The next step was to tie this result in with some known method for producing solid, stable, calcium hypochlorite.

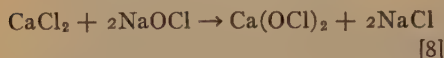
PRODUCTION OF HYPOCHLORITE

Theoretically, conversion of chlorine to hypochlorite may be expressed by the reactions:



It is well known that the chemical instability of ordinary lime bleach is due, at

least in large part, to the presence of CaCl_2 , while sodium hypochlorite is so unstable that it cannot be used commercially in dry form. Some 15 years ago research workers discovered that stable dry bleach (essentially calcium hypochlorite) could be made by metathesis according to the reaction



in which unstable NaOCl from reaction 7 and the detrimental CaCl_2 from reaction 6 are converted into stable $\text{Ca}(\text{OCl})_2$ and harmless NaCl . In the interest of the war effort, this reaction was adopted as the basis of our further progress toward production of stable bleach of high available chlorine content. The process thus involved separate production of chlorinated lime and caustic soda solutions, and mixing these in suitable proportions to bring about reaction 8.

The next step was to produce a dry product, for which purpose spray drying was adopted following successful trials in a spray drier of commercial size, using liquor made in pilot-plant absorbers at Painesville. The product, a fine powder containing more than 40 per cent available chlorine, appeared to meet all specifications then known to us, for use by the armed services.

On the basis of these pilot-plant results, we were requested to build, as an extension of the magnesium plant, a hypochlorite plant designed to convert to solid calcium hypochlorite as much as possible of the by-product chlorine. This meant a capacity of about 120 tons of finished product per day—by far the largest hypochlorite plant ever built or probably ever contemplated. The process to be used, while old in a chemical sense, departed widely from previous practice and involved pioneering steps of a critical nature. For example, removal of salt from the sodium hypo-

chlorite liquor presented a difficult problem, which was solved by field trials with a continuous centrifuge of commercial size. The design of spray driers for so huge a capacity of a thermally unstable compound presented special problems. Final design called for three such driers, coal fired, each with an evaporating capacity of about 90 tons of water per day, drying the product to about 1 per cent moisture content by direct contact with indirectly heated air. It required considerable courage to build such a pioneering plant without elaborate pilot-plant study, but time pressed, and the decision to go ahead was taken along the lines of Farragut's famous "Damn the torpedoes; full speed ahead."

An interesting feature of the program was the completion, well in advance of the rest of the plant, of one of the four full-scale absorption-tower units, together with a pilot-plant spray drier. The purpose was twofold—to turn out product in sufficient volume for field tests by the Army, and to train operators well in advance of commercial production. Thus final pilot-plant work and construction of the plant were telescoped into the same period of time.

Meanwhile, additional information regarding newly established specifications for the product was disclosed, and it became evident that the product would have to be altered somewhat both chemically and physically. Details of such requirements cannot be stated here, but they necessitated a further urgent research and pilot-plant study for the modification of the product itself to meet the new specifications of the armed services. This study was only just under way when the plant began commercial operation in June 1944, with one of four absorption units and one of three spray driers in use. To the credit of the designing engineers and suppliers of equipment, very little serious trouble developed, though the normal

birth pains of a new plant, using a new process, producing a new product, were encountered.

At the time of writing, in late August 1944, the plant is producing commercially,

modify the product as to meet specifications for other uses. Thus successful conversion of the otherwise waste cell gas into a needed wartime product is an accomplished fact. The flowsheet is shown in Fig. 3.

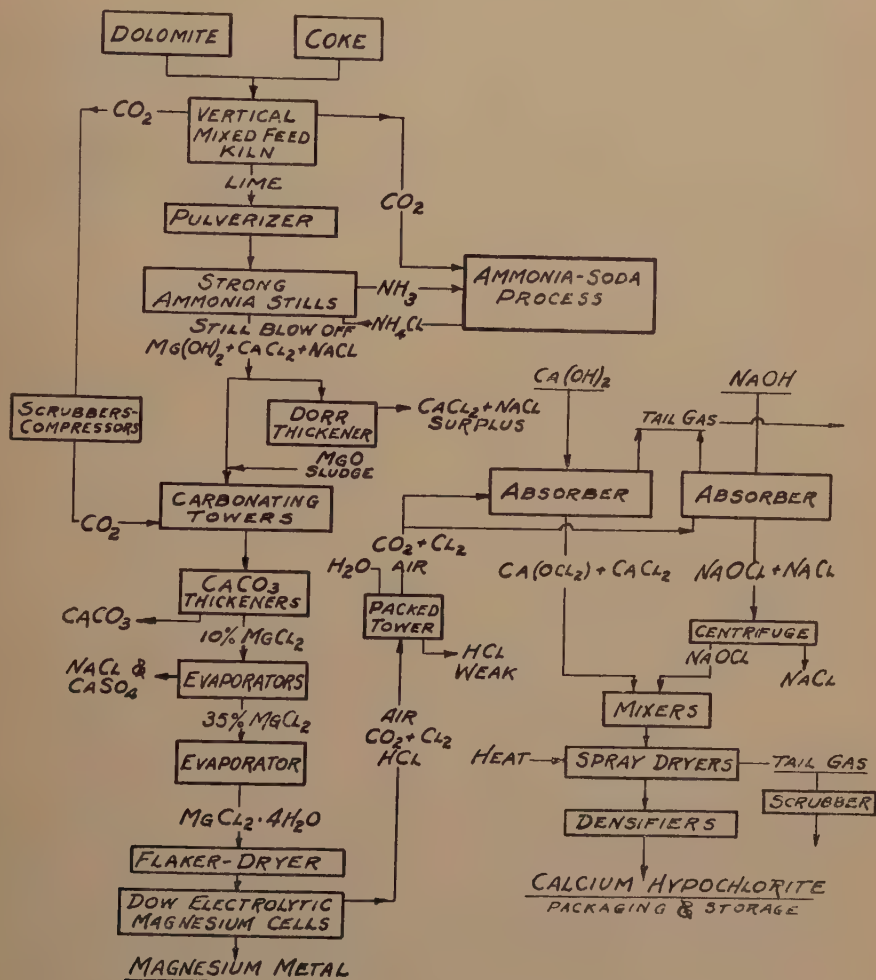


FIG. 3.—FLOWSHEET FOR PRODUCTION OF CALCIUM HYPOCHLORITE.

solid, stable calcium hypochlorite acceptable for certain purposes, and equipment is being installed* that is expected so to

*At the time of going to press (January 1945) this equipment is in successful commercial operation.

CONCLUSION

All in all, the magnesium operation at Painesville is thus not without interest. It is the only plant in which magnesium chloride is made from dolomite as an

adjunct of the ammonia-soda process, and the only one in which the by-product chlorine is recovered for use in the manufacture of another wartime chemical. Surprisingly enough, the over-all economics of the plant, in spite of the high cost of the public-utility power, are sound, at least for war purposes. What the future holds for such a plant in the postwar period is only a small part of the whole postwar problem—he would be bold indeed who would hazard anything more than a guess. Meanwhile, it has served its

purpose as an aid to winning the war, and with that we are content.

ACKNOWLEDGMENT

The successful completion of this project is the result of cooperative effort by many chemists, engineers, executives and operating personnel under unusually trying conditions. The authors, finding it impossible to select individuals to whom special acknowledgment should be made, pay tribute to all those members of the Diamond Alkali Co. and Diamond Magnesium Co. organizations who by their efforts contributed to its success.

The Plant of the Dow Magnesium Corporation at Velasco, Texas

By C. M. SHIGLEY*

THE record of the largest magnesium plant in the country utilizing sea water as a primary raw material stands as another victory in the struggle for large-scale production of pure chemical elements from the oceans.

Bromine was the first element to be economically and commercially recovered when, in 1933, a six million pound per year unit was built on the Atlantic Coast near Wilmington, North Carolina, by the Ethyl-Dow Chemical Co.¹ The bromine was reacted with ethylene to produce ethylene dibromide, a necessary associate of tetraethyl lead in ethyl antiknock fluid. Within eight years that plant was doubled and redoubled, and another large unit was put into operation at Freeport, Texas, taking bromine from the Gulf of Mexico.

In 1940, in fortunate anticipation of the impending demand for magnesium and the limitations of the production from natural brines, the Dow Chemical Co. turned again to the sea, and designed and erected a plant at Freeport to produce 18,000,000 lb. of magnesium per year from sea water.² In March 1941, two months after the new plant had been put into successful operation, construction of an 18,000,000-lb. Government-financed addition was started. Late in 1941, as a part of the \$400,000,000 defense program intended to produce 600,000,000 to 700,000,000 lb. of magnesium per year, Dow was asked to build and operate for the Government a 72,000-

000-lb. plant near its original plant at Freeport.

Within a few days after the Japanese made their attack at Pearl Harbor, preparation of a site was started at Velasco, Texas, for the construction of the Texas plant of the Dow Magnesium Corporation—the largest known magnesium plant utilizing sea water as its raw material. Less than six months after the first piling was driven, urgently needed magnesium was in steady production. Five months later, the plant had exceeded its rated capacity. It remained above rated production until the general magnesium curtailment was applied to Government-owned plants in September 1944.

Credit for the construction and operation record of the Dow magnesium plant must be divided among the efforts of a very determined group of men, an extremely favorable location, and a simple process. It is with the two latter aspects of the plant that this article will deal.

The site for the new enterprise was chosen near Velasco, Texas, on property bordering the Brazos River at a point approximately 6 miles inland from the original magnesium plant and 7 miles inland from the Freeport Harbor on the Gulf of Mexico. This location was far enough away from the operating units to reduce both interference from construction and the vulnerability of closely bunched manufacturing operations to the then feared air attack. Yet the distance inland was not too great for the economical construction of a barge canal from the harbor to serve both the transportation of raw

Manuscript received at the office of the Institute Nov. 16, 1944. Issued as TP 1845 in METALS TECHNOLOGY April 1945.

* Texas Division, The Dow Magnesium Corporation, Velasco, Texas.

¹ References are at the end of the paper.

materials and the supply of sea water for processing and cooling. From the site, the Brazos River conveniently flowed to the Gulf at a point 7 miles south of the harbor,

months of 1942 to become the buildings and equipment required to manufacture the 72,000,000 lb. of magnesium per year from the sea.

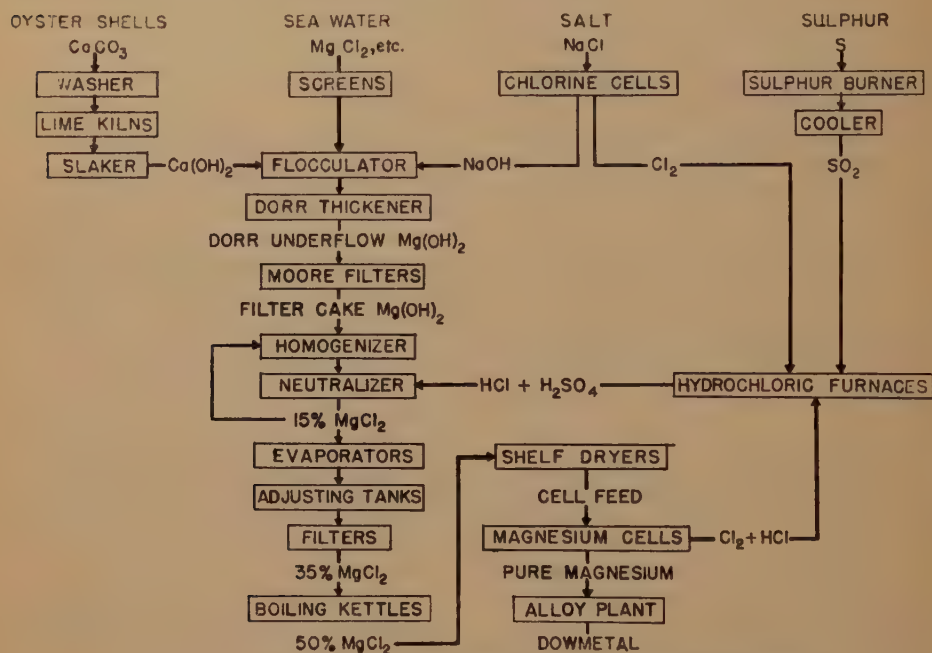


FIG. 1.—FLOWSHEET OF THE DOW SEA-WATER MAGNESIUM PROCESS.

providing a means of disposal of processed ocean water with little danger of recycling. In addition to readily developed facilities for the supply and wasting of the sea water, the location was in close proximity to all other major raw materials required. Oyster shells for the manufacture of lime were available by barge from Galveston Bay, approximately 40 miles distant; salt, used for the manufacture of chlorine, was obtainable at the huge Bryan Mound salt dome, only 8 miles distant; sulphur was available from Hoskins Mound, only 10 miles away, and natural gas for fuel and power was obtainable in large quantities from fields within a radius of 30 miles. It was to this naturally favorable site that approximately 12,000 carloads of construction materials moved in the first six

The rapid construction and reliable operation of the new plant has been a triumph more for large-scale engineering than for chemical wizardry. There is approximately 1000 lb. of magnesium in every 1,000,000 lb. of Gulf water. The recovery of the magnesium consists merely of an economical combination of simple, and in most cases, well-known unit processes, accomplishing the progressive elimination of the 999,000 lb. of water and other materials. The process as a whole should perhaps be regarded not as the extraction of magnesium from sea water but as the extraction of sea water from magnesium.

Fig. 1 presents a simplified materials flowsheet showing the steps by which the extraction is successfully effected.

DECANTATION

Referring to the first step for a closer inspection of the plant and the process, it is quite obvious that an assured supply of uncontaminated Gulf water of high salinity is a primary consideration. The location of the site at the apex of a triangle having one leg along the barge canal supplying the water, one leg along the Brazos River carrying the effluent to the Gulf, and its base as the 7-mile stretch of Gulf coast between inlet and outlet, provides reasonable assurance against recycling of the previously processed water. The protection of the incoming brine against excessive dilution from local fresh-water run-off and from the Brazos River is afforded by the installation of a suspended skimmer gate at the entrance to the barge canal. The gate, extending 20 ft. below the water surface, very effectively prevents the ingress of the stratified surface fresh water at all times except when it has to be lowered to permit passage of raw-material barges.

Passing under the skimmer gate and through the 7 miles of canal to the plant proper, the water is screened through standard traveling trash screens, to remove fish and large debris. Five 71,000-gal.-per-min. pumps then deliver it through horizontal cylindrical screens to a large earthen flume extending the full width of the plant. Here it is chlorinated to an excess of 0.5 p.p.m. to curb marine growth. From the flume, other pumps supply the cooling water under the pressure and volume conditions required, and furnish process water to the first or decantation step of the magnesium recovery.

Oyster shells, dredged from Galveston Bay and barged to the plant, are unloaded by crane, washed to remove sand and debris, and fed directly or from storage to three horizontal rotary kilns, each 9 ft. 6 in. in diameter by 265 ft. long and having a nominal capacity of 185 tons of lime per day. The CaCO_3 of the shells is converted to high-purity CaO by burning at a tem-

perature of 1200° to 1400°C . The white-hot product falls into a rotary slaker, where it is quenched with water and slaked to form a water suspension of $\text{Ca}(\text{OH})_2$. The suspension is pumped to 200-ft. diameter Dorr settling tanks, in which the hydroxide drops out as a heavy slurry while the clears are recycled to the slakers. The $\text{Ca}(\text{OH})_2$ underflow is mixed with a small amount of by-product caustic and then is diluted to a constant concentration for ease of control.

The sea water from the central flume is pumped through a constant-head tank into a reinforced-concrete flocculator tank, where it is agitated with an excess of $\text{Ca}(\text{OH})_2$. Precise control of the mixing converts the soluble MgCl_2 of the sea water into a rapid settling, easily filterable precipitate of $\text{Mg}(\text{OH})_2$ relatively free from troublesome boron.³

The treated sea water flows by gravity from the flocculator through a reinforced-concrete duct to the center of one of four 500-ft.-diameter Dorr settling tanks of earth-dike construction with gunited surfaces. As the liquid flows radially from the center, the $\text{Mg}(\text{OH})_2$ settles out and the spent sea water overflows into the peripheral launders and is carried away to the central disposal system. A Dorr thickening mechanism in each quadrant of the large tank plows the thick magnesium hydroxide slurry to the center of the quadrant, whence it is pumped to a central sump and forwarded to storage.

This first step removes approximately 98 per cent of the water and other materials with which the magnesium was originally associated in the sea water, and provides a 12 per cent $\text{Mg}(\text{OH})_2$ slurry of the appearance and consistency of thick cream, readily pumpable, and containing practically all of the magnesium and most of the calcium and bicarbonates (now carbonates) of the sea water. Fig. 2 indicates graphically the accomplishment of the decantation as well as the subsequent steps in the elimination process.

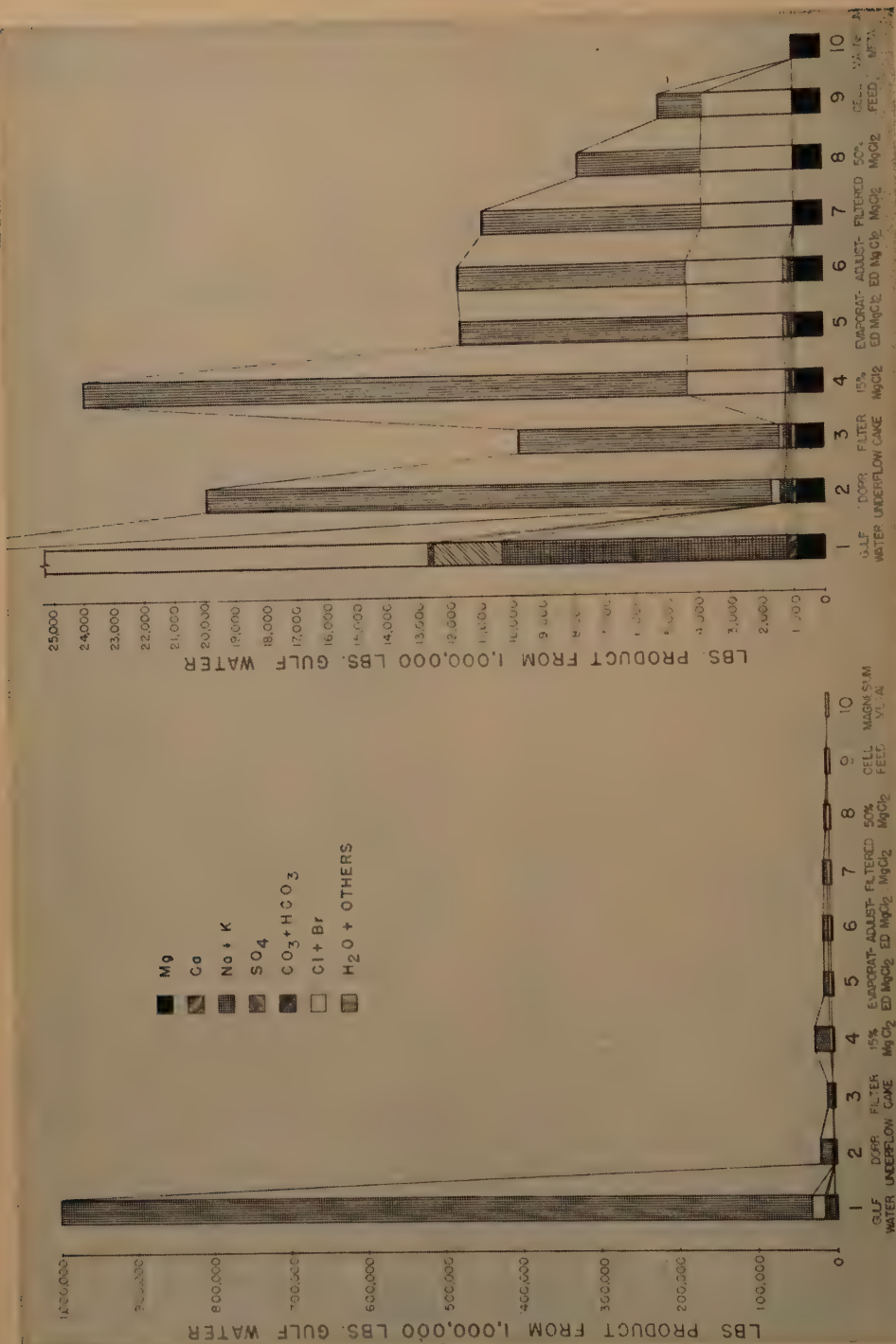


FIG. 2.—INTERMEDIATE PRODUCTS OF THE DOW SEA-WATER MAGNESIUM PROCESS.

FILTRATION

Nineteen Moore leaf-type filters provide the filtration equipment for the $\text{Mg}(\text{OH})_2$. Each filter unit consists of a "basket" constructed of parallel H-beams 78 ft. long, from which are suspended 100 filter leaves individually connected to a central suction header. The individual leaves are filter cloth envelopes 5 by 8 ft., having their sides held apart by internal spacer strips. Each filter basket is lowered into a long, narrow horizontal pit filled with the $\text{Mg}(\text{OH})_2$ slurry. Filtrate pumps, supplemented by a vacuum system, dewater the slurry and in a period of 2 hr. deposit a 1 to 2-in. cake of the hydroxide on the outside of the filter cloth. The basket, weighing loaded nearly 60 tons, is hoisted from its pit by means of a traveling crane, and transported to one of three dump tanks similar to the load pits and located near them. Air pressure applied to the header flexes the filter leaves, discharging the cake into the dump pit, and the basket is returned to its filter pit for another load.

In the filtration step, approximately half of the remaining water and soluble materials are removed from the $\text{Mg}(\text{OH})_2$. The calcium and carbonate impurities remain practically unaffected.

NEUTRALIZATION

The filter cake, containing 25 per cent of $\text{Mg}(\text{OH})_2$ by weight, is mixed with dilute MgCl_2 and "creamed" to a pumpable slurry by agitation and pumping through an homogenizer. The mixture is then delivered to the neutralizers for reaction with recycled HCl.

Each neutralizer consists of two 12 by 16-ft. brick-lined tanks in series, equipped with rubber-covered propellor-type agitators. All of the $\text{Mg}(\text{OH})_2$ and three fourths of the required acid are added to the first neutralizer. The acid necessary to complete the conversion of $\text{Mg}(\text{OH})_2$ to MgCl_2 is added in automatically controlled quantity to the second tank. The glass

electrode pH is maintained at 6.5. The carbonates are decomposed by the acid with liberation of CO_2 , while the total sulphates are increased by a small amount of H_2SO_4 mixed with the HCl.

Part of the resultant 15 per cent magnesium chloride solution is returned to the dump pits for creaming; the remainder is pumped to one of the three 100 by 40-ft. steel storage tanks.

The amount of water associated with the magnesium is increased by this step in the process, but this is an inevitable consequence of the economical recycling of the chlorine from MgCl_2 to Cl_2 to HCl and back to MgCl_2 again.

EVAPORATION

It is next necessary to evaporate the 15 per cent MgCl_2 solution as one step in the elimination of water and to reduce the solubility of NaCl to the limit required by the cell-feed composition.

The severe scaling of tubular evaporators because of the small amount of CaSO_4 present makes it necessary to use a direct method of heating. The evaporators used in this case are an adaptation of the submerged combustion principle described by Douglass.⁴ There are four units, operating independently. Each unit consists of four covered brick-lined concrete evaporator pots 12 ft. in diameter by 10 ft. deep, vented to a common quench tower equipped with an electrostatic precipitator. A 4000-cu. ft. per min. positive displacement blower opposite each pot delivers air at 5 lb. pressure to a mixing chamber. Carefully controlled natural gas is admitted to maintain an air to gas ratio of between 9 to 1 and 11 to 1. The mixture is piped through the reinforced-concrete cover and delivered to a 16-in. diameter bell-shaped burner extending 4 ft. below the surface of the liquid. Upon ignition, continuous burning is maintained in the bottom of the burner, and the hot combustion products pass through the MgCl_2 solution,

yielding approximately 75 per cent of the available heat in evaporative effect. The hot gases are vented from the individual pots through 3-ft. diameter pipes to a header leading to a 20-ft. diameter quench tower 50 ft. high. Here, sea-water sprays, supplemented by a shallow section of drip-point tile packing, reduce the temperature of the vent gas from 110° to 40°C . and scrub out most of the entrained MgCl_2 and a small part of the MgO . The latter, which is formed in small amount by thermal decomposition of the MgCl_2 at local hot spots in the evaporators, requires electrostatic removal to prevent a fog nuisance. At the top of each quench tower, 80 12-in. diameter precipitator tubes, operating at an electrode voltage of 75,000 volts, effect a 90 per cent removal of the fog.

The 15 per cent MgCl_2 liquor is fed into the end evaporator pot of a unit, passes through each of the other pots in turn, and is withdrawn from the fourth at the rate required to maintain the desired product concentration. The hot liquor passes to a vacuum cooler where evaporative cooling reduces the temperature to approximately 50°C . Elimination of more than 60 per cent of the water in the feed is thus effected, and the magnesium chloride concentration is increased to 35 per cent by weight, at which point the solubility of the sodium chloride is reduced to the limit required by the cell-feed specifications.

ADJUSTMENT

The cooled evaporator product is forwarded to brick-lined adjustment and retention tanks. Here a mixture of MgSO_4 and MgCl_2 in solution, made by the reaction of creamed hydrate with H_2SO_4 , is added in the amount calculated to precipitate unwanted calcium as insoluble CaSO_4 . The carefully adjusted liquor is held for 24 hr. to reduce the supersaturation of CaSO_4 , and is then pumped to the filters.

FILTRATION

The adjusted evaporator product is first filtered through one of two Moore filters identical with those used for the earlier $\text{Mg}(\text{OH})_2$ filtration. The filter cake, consisting primarily of NaCl and CaSO_4 , is washed on the filter to remove as much as possible of the MgCl_2 solution and is then sluiced off and discarded.

The filtrate is pumped through Sperry plate and frame presses for a final polish, and is stored in brick-lined steel tanks.

At this stage of the process, all of the unwanted ingredients of the sea water except the last of the water itself have been eliminated. The magnesium is now associated with only 11 times its weight of other elements, whereas in the original sea water the ratio was 1 to 999.

EVAPORATION

The peculiar characteristics of magnesium chloride prevent use of normal methods of dehydration, which would otherwise be expected to attain the dry solid form. In the first place, the boiling-point curve approaches the freezing-point curve as the MgCl_2 concentration is increased (Fig. 3). The practical limit of handling MgCl_2 as a liquid is reached at a concentration between 50 and 55 per cent. Second, solid hydrated MgCl_2 at a concentration below 68 per cent fuses easily at economical drying rates. Third, solid MgCl_2 reacts with its water of crystallization at elevated temperatures and at high ratios of magnesium chloride and water to produce MgO and HCl .

Elimination of the water in excess of that tolerable in the electrolytic cell is accomplished therefore in two steps. The filtered 35 per cent MgCl_2 solution is first evaporated to a concentration of 50 per cent in any of nine open-top brick-lined steel boiling kettles, each of which is 16 ft. in diameter by 12 ft. high. The heating is done by 400-lb. steam in submerged Inconel or heat-treated 347 stainless-

steel coils. The previous removal of CaSO_4 and NaCl reduces the tube scaling to a dust removal, and blow it into a ring-packed scrubber tower 20 ft. in diameter

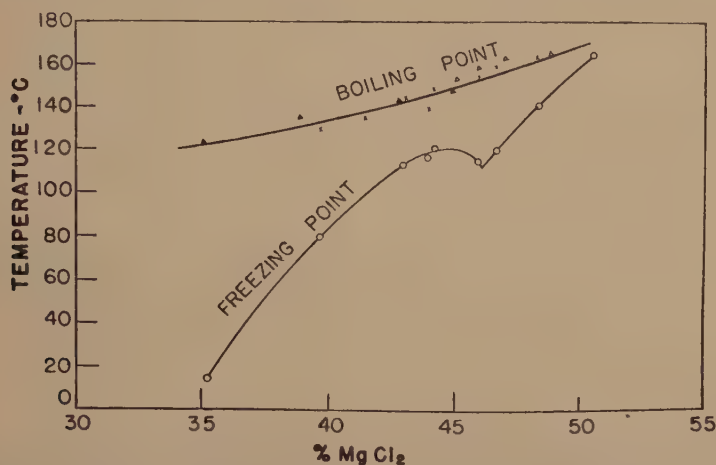


FIG. 3.—FREEZING-POINT AND BOILING-POINT CURVES FOR MAGNESIUM CHLORIDE.

minimum. Nearly one half of the remaining water is removed by this simple operation.

DRYING

The 50 per cent MgCl_2 liquor, at a temperature of approximately 170°C . is pumped through steam-traced Monel lines to one of three shelf driers. The liquid is sprayed on six times its weight of previously dried solid in a horizontal rotary mixer 10 ft. in diameter by 60-ft. long. A white, granular solid slightly above the critical 68 per cent limit is obtained. This is elevated to the top and center of the drier proper.

The latter is an insulated cylindrical steel chamber, 50 ft. in diameter and 50 ft. high. Twelve equally spaced horizontal shelves are provided with raker arms turned by a central rabble shaft at a speed of 1 r.p.m. The upper 10 shelves are provided with a common hot-air recirculation system directly fired with natural gas. The lower two shelves have a similar system, providing somewhat higher air temperatures. Dual vent fans withdrawing air from the recycle duct pull the dust-laden exhaust through hot cyclone separators for

by 60 ft. high, for recovery of MgCl_2 and HCl before venting to the atmosphere.

The flow of solid granular MgCl_2 is split at the top of the drier into 10 equal parts, each of which is piped down to the center of one of the 10 upper shelves. As the raker arms move the material radially toward the edge of the shelf, it is dried by circulating hot air at a temperature of 250° to 300°C . At the outer edge of the shelf the material is scooped into a chute and passed to a parting box, which recycles 90 per cent to the mixer and forwards the remainder to the two lower shelves. At the latter point the drying proceeds at an air temperature of 450°C . and produces a free-flowing white, granular solid of the approximate composition $\text{MgCl}_2 \cdot 1\frac{1}{2}\text{H}_2\text{O}$. This hygroscopic material is transported by drag chain conveyors either to storage tanks or directly to the cells.

While this step in the process removes only 0.3 per cent of the original H_2O in the magnesium-bearing sea water, it is highly significant in that it produces a solid and dries it to the limits of the electrolytic cell requirement with a minimum of fusing and decomposition.

ELECTROLYSIS

The Dow process employed in the electrolysis of the magnesium chloride so prepared has been thoroughly described by R. M. Hunter.⁵

The magnesium cells section of the Velasco plant consists of eight identical buildings housing twenty-seven cells each. The buildings are arranged in groups of four to form two pot lines of 108 cells, of which 100 normally operate in series. Each pot line is served by six 10,000-amp., 650-volt, Westinghouse Ignitron mercury-arc rectifiers. The buildings themselves are constructed of brick, steel, impregnated Transite and wood, carefully designed to minimize stray currents and electric shock hazards. Adequate ventilation, approximately 60,000 cu. ft. per min. per cell, is provided by 13 120,000-cu. ft. per min. propeller-type exhaust fans at the top of each building.

Each cell is a bathtub-shaped pot 5 ft. wide, 11 ft. long and 6 ft. deep, set at operating floor level in a gas-fired brick setting. Twenty-two graphite electrodes 8 in. in diameter and 9 ft. long are suspended through an arched refractory cell cover. Electrical connection to the pot is provided by solidly welded copper bus bars. Connection to the graphite electrodes is accomplished by flexible copper cables. Access holes at the front of the cell cover permit introduction of tools to dip the metal and to service the cell.

Each operating cell is full of a fused salt mixture composed approximately of 25 per cent MgCl_2 , 15 per cent CaCl_2 , and 60 per cent NaCl , at a temperature maintained between 700° and 750°C. by controlled gas firing. Cell feed is added continuously, except during the periodic dipping or servicing of the cell, and at such a rate as to maintain the proper bath level. The feed is melted by the heat of the bath, and the residual water is evaporated. The desired bath composition is maintained by adjustment of the CaCl_2 and NaCl in the

cell feed to balance the quantities removed during the regular cleaning of the cell.

Passage of the current between the graphite anode and the steel-pot cathode electrolyzes the MgCl_2 of the bath, yielding elemental magnesium and chlorine. The molten magnesium rises to the top of the cell, where it is trapped by inverted troughs and directed to metal storage wells at the front of the cell. The metal is hand-dipped from the wells three to four times a day and cast into standard 18-lb. notched ingots. The purity of the magnesium so obtained is 99.9 per cent or better. The current efficiency is 75 to 80 per cent, and the direct-current power requirement is approximately 8 kw. hr. per lb. of magnesium produced.

The hot Cl_2 gas, together with inleaking air and some HCl produced by the reaction of Cl_2 with water, is pulled from the top of the cell, quenched for ease of handling, and piped to the hydrochloric acid plant

HYDROCHLORIC ACID PLANT

Eight regenerative hydrochloric furnaces convert the greater part of the free Cl_2 of the magnesium-cell gas to HCl by reaction with steam and natural gas. The unconverted Cl_2 is reduced by the controlled addition of SO_2 supplied by Glens Falls rotary sulphur burners. The acid gases are absorbed by water in multiple ring-packed scrubber towers, yielding a solution containing 20 per cent HCl and a small amount of H_2SO_4 . The mixed acids are returned to the neutralizers for the reaction with $\text{Mg}(\text{OH})_2$ as previously described.

The inevitable small loss of chlorine in one form or another during the feed preparation, electrolysis, and acid recovery, is replaced by addition of Cl_2 to the magnesium cell gas. Approximately $\frac{1}{2}$ lb. of Cl_2 is required per pound of magnesium metal produced, under present operating conditions. To supply the chlorine, a saturated NaCl solution is pumped from the $\frac{1}{2}$ -mile deep salt well at Bryan Mound.

After pretreatment, the solution is electrolyzed in standard Hooker type S cells, yielding make-up Cl_2 as required, and an equivalent amount of dilute NaOH . The latter is evaporated for partial NaCl recovery, and then pumped to the sea-water treating system, where it supplements Ca(OH)_2 in the Mg(OH)_2 precipitation.

ALLOYING

The pure magnesium in the familiar ingot form may be shipped as such or may be alloyed to any one of several commercially used magnesium alloys.

The Velasco plant has alloy facilities sufficient to process the entire magnesium-cell output. The equipment consists principally of three gas-fired reverberatory furnaces, nine alloying pots, and six continuous-casting conveyors. These are housed in a fireproof brick and concrete building 100 ft. wide and 300 ft. long, ventilated at the roof by four propeller-type fans having a capacity of 120,000 cu. ft. per min. each.

In the alloying operation, pure magnesium metal is melted in a reverberatory furnace. The molten metal at 700°C . is pumped to heated steel pots where the alloying elements, principally aluminum, zinc and manganese, are added. After rapid spectrographic analysis, the alloy may be pumped into a continuous-casting conveyor producing 25-lb. alloy ingots, or delivered into fixed molds producing extrusion billets. The 25-lb. ingots are storage-cooled and shipped directly to the consumer as cast, while the billets are scalped before shipment and the turnings returned to the alloy pots.

GENERAL FACILITIES

Description of the Velasco plant would not be complete without mention of some

of the other facilities built in support of the magnesium-production units. These include a 115,000-kw. steam-power plant to supply the demands of the process, a general analytical laboratory for process control, complete service and shop facilities, a plant-operated cafeteria, a trailer camp, and a modern 52-bed hospital for the benefit of workers in the area and their families.

SUMMARY

The unquestioned weight advantage of the magnesium alloys, coupled with their ease of fabrication and good corrosion resistance, make the future of magnesium look very bright in a world of motion. The past, slow, hard struggle of this capable light metal will be considerably eased by the well demonstrated feasibility of its recovery from sea water. For what other competing materials can boast a plant location providing all the major process requirements within such a short radius, a simple process where most of the intermediate materials can be handled by pumping, and a supply of primary raw material, which, like the sea, flows of its own accord and in unlimited quantity to the plant's very doorstep?

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Pilot-plant Production of Electrolytic Magnesium from Magnesite

By R. R. LLOYD,* MEMBER, C. K. STODDARD,† K. L. MATTINGLY,‡ E. T. LEIDIGH,§ AND
R. G. KNICKERBOCKER,|| MEMBER A.I.M.E.

DURING July 1941, a study was initiated at the Boulder City Experiment Station of the Bureau of Mines on proposed methods for the production of magnesium metal. The major emphasis was placed upon development of a process that required minimum reliance upon the sale or utilization of by-products to meet economic competition from processes already in operation. It was felt that only through the development of such a process could the nation's vast resources of dolomite and low-grade magnesite that are contiguous to large blocks of firm power be properly utilized.

During the course of exploratory tests on electrolytic and electrothermic processes, it was noted that fused magnesium chloride would dissolve appreciable quantities of magnesium oxide in the presence of small amounts of boric oxide. The use of such a solution in an electrolytic cell employing a graphite anode and a steel cathode caused the deposition of magnesium at the cathode and the evolution of carbon oxides at the anode with minimal amounts of chlorine. The original results were

sufficiently encouraging to justify further investigation on an enlarged scale, since the process seemed to present advantages over other proposed processes^{1,2} for the direct use of magnesium oxide in a fused chloride electrolyte. When work on a larger scale was initiated it was found that the addition of boric oxide to the electrolyte resulted in dispersion of metal and constantly decreasing current efficiency. However, by this time solubility studies had shown that magnesium oxide was sufficiently soluble in magnesium chloride melts containing no boric oxide to effect the same anode reactions, and development work was continued.

Over two years of development work have been carried out, and considerable work remains to be done. It is desired to emphasize the fact that many of the difficulties met require a long period of continuous operation before they become serious enough to affect operation of the cell.

ACKNOWLEDGMENTS

This paper is one of many reporting on various aspects of the Bureau of Mines' program initiated in August 1939 by passage of the Strategic Minerals Act the scope of which was greatly expanded by subsequent legislation.

Some of these papers are published as war minerals reports, others as bulletins, technical papers, reports of investigations

Presented by permission of the Director, Bureau of Mines, U. S. Department of the Interior. Manuscript received at the office of the Institute Nov. 15, 1945. Issued as TP 1848 in METALS TECHNOLOGY April 1945.

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¹ References are at the end of the paper.

and information circulars of the Bureau of Mines or in technical journals.

The Bureau's program at first included separate investigations by the Mining and Metallurgical Divisions, but these were consolidated under Assistant Director R. S. Dean, beginning July 1, 1942. Mining and metallurgical investigations were carried on in three regional organizations more closely integrated thereafter by a staff of specialists, who reviewed findings made in the field and in Bureau laboratories, considered proposals for additional work, revised reports for publication, and served as advisors to the Assistant Director.

With respect to this report, special acknowledgment is due to C. E. McCarthy, of the Aluminum-Magnesium Division, for extensive revision of the report, and to him and K. K. Kelley, of the Berkeley Station, for assistance given the authors in the kinetic and thermodynamic interpretation of the results. Acknowledgment is also made to H. W. St. Clair, Assistant Regional Engineer, Western Region; to P. M. Ambrose, Chief, Aluminum-Magnesium Division; to S. S. Lawrence and J. Perlman, of the Boulder City Station, for special analytical work; to S. F. Ravitz, P. P. Zapponi and B. Cartwright, of the Salt Lake City Station, for their work on solubility relationships, and to E. V. Potter and R. W. Huber, of Salt Lake City, for the data on the conductivity and density of fused salt.

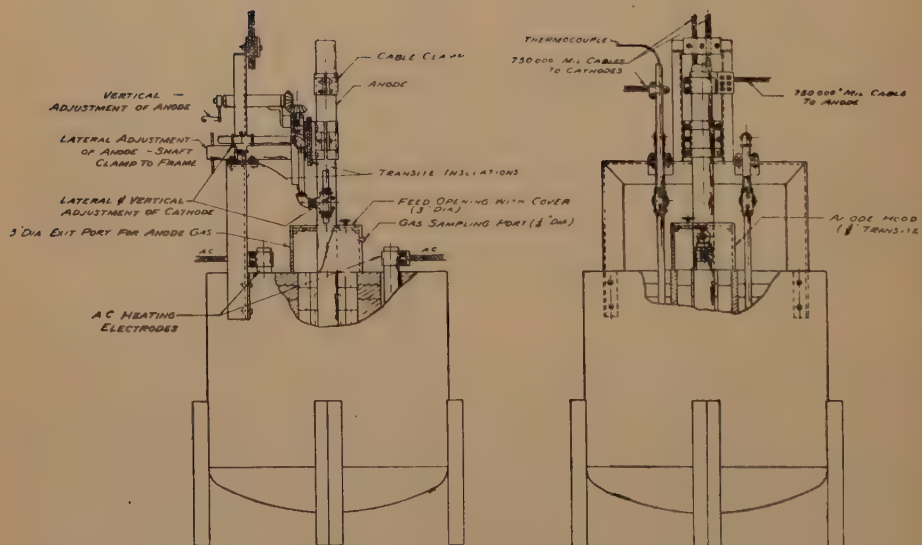
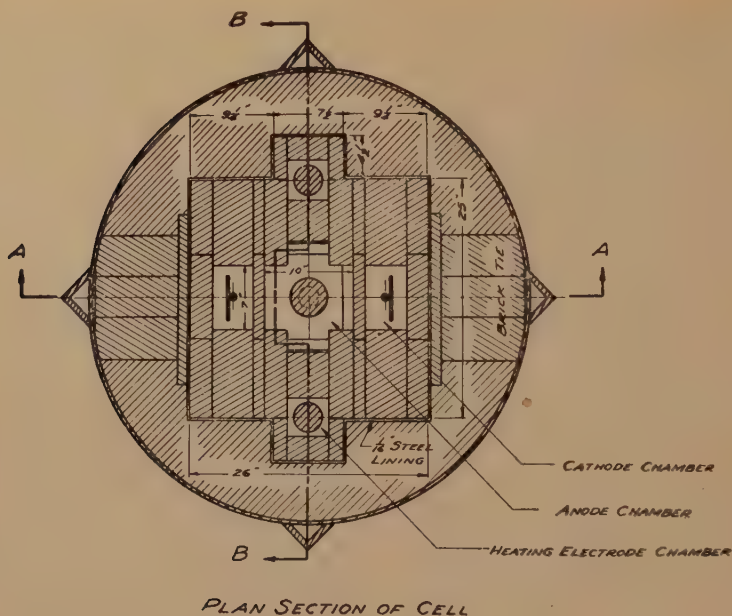
CONSTRUCTION OF CELLS USED FOR ELECTROLYSIS

After completion of miscellaneous laboratory tests in externally heated iron pots, using steel or molten lead cathodes, small-scale work was carried out in the cell shown in Fig. 1. This was lined with firebrick and held 125 to 150 lb. of electrolyte. It was operated on a direct current of 350 to 700 amp.; auxiliary heating was

provided by two alternating-current electrodes projecting from the brickwork near the bottom of the cell. Tests were also made with minor modifications of this construction.

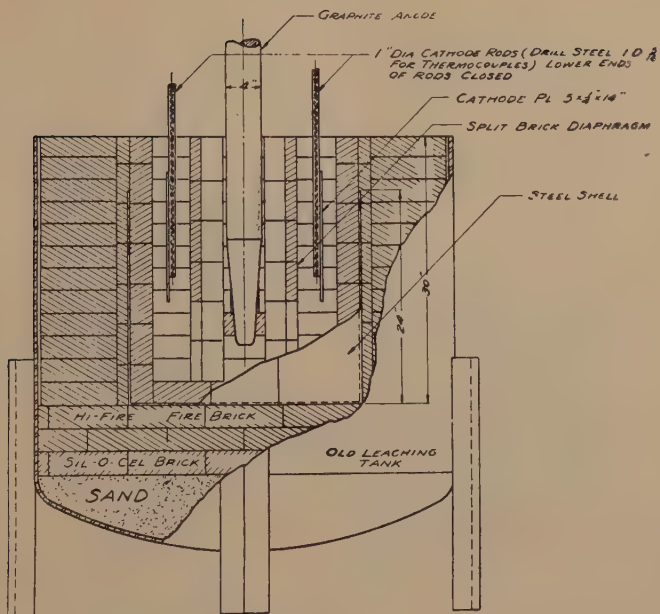
An 8000-amp. pilot cell was constructed on approximately the same principles as the test cell shown in Fig. 1, except that no auxiliary heating electrodes were provided. This cell failed after six weeks operation, because of inadequate methods of construction, which permitted the electrolyte to attack the steel shell.

A second cell was constructed, with a thicker lining of better construction and an uninsulated outer steel shell. This cell, shown in Fig. 2, operated for nearly 12 months and was in good condition when the tests were completed. The cut-away drawing shows the interior electrodes and cell construction, as well as the superstructure supporting the electrodes and the feeders. The cell proper consists of a welded-steel box lined with vitrified, acid-proof brick having a porosity of less than 2 per cent, set in a sodium silicate-silica-type mortar. The rectangular cavity inside the brick lining, 62 in. long, 36 in. wide and 45 in. deep, is divided longitudinally into two outside compartments, or cathode chambers, and one inner compartment, or anode chamber, by fused-alumina (90 per cent) partitions, 24 by 12 in., placed in the upper part of the cavity. The partitions were supported 22 in. above the cell floor by brick piers at the panel joints, leaving an opening below for the passage of current from anode to cathode. After four months, the original flint firebrick piers failed and were replaced by 90 per cent alumina brick of the same composition as the partitions, which had not suffered any appreciable corrosion. By sloping the bottom portion of the side walls to the cell floor, sharp corners were eliminated, in an effort to minimize accumulation of sludge and freezing of electrolyte.

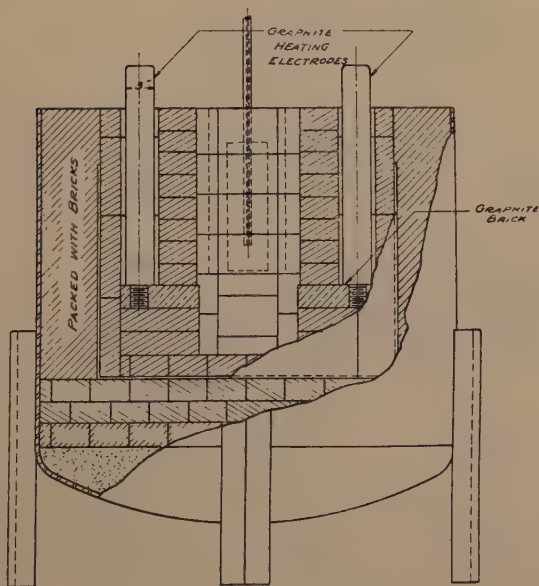


ASSEMBLY DETAILS OF SUPPORTS FOR ANODE & CATHODES

FIG. 1.—SMALL CELL USED FOR PRELIMINARY ELECTROLYSIS INVESTIGATION

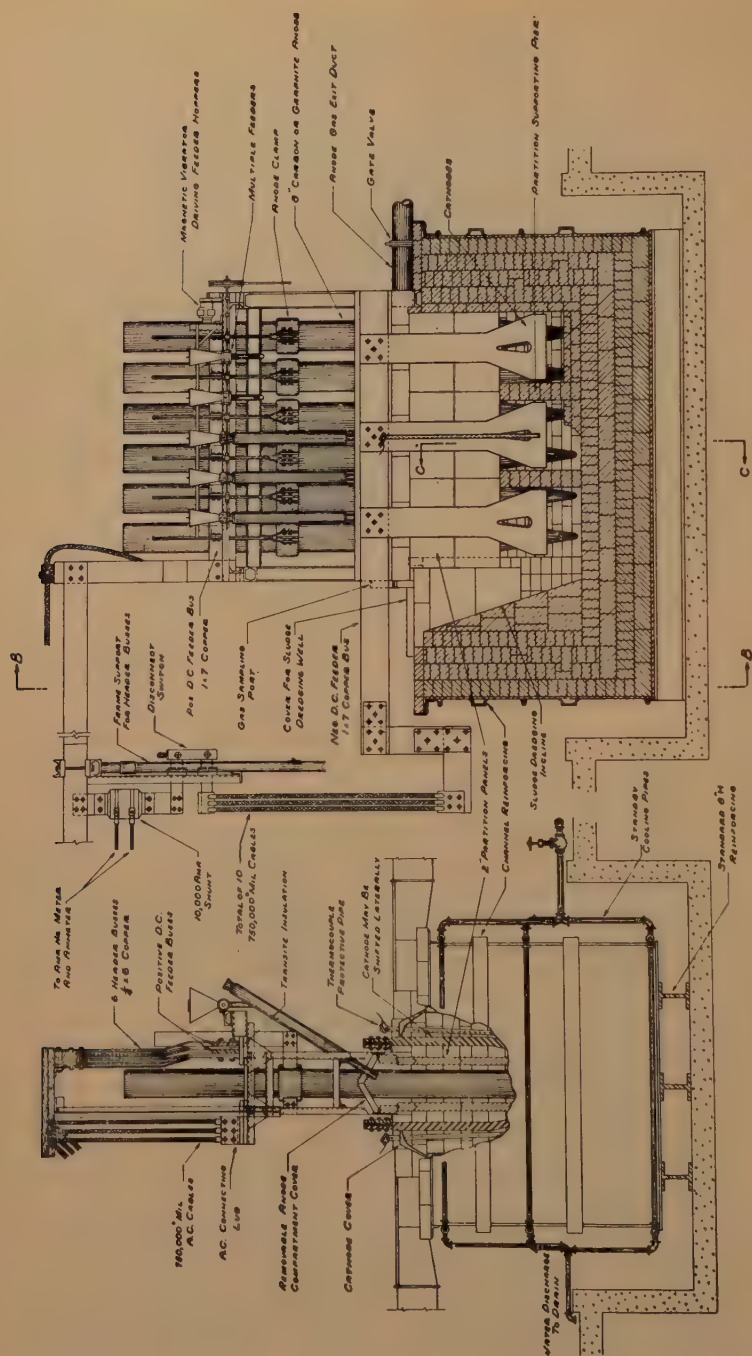


SECTION A-A



SECTION B-B

FIG. 1.—SEE OPPOSITE PAGE FOR DESCRIPTIVE LEGEND.



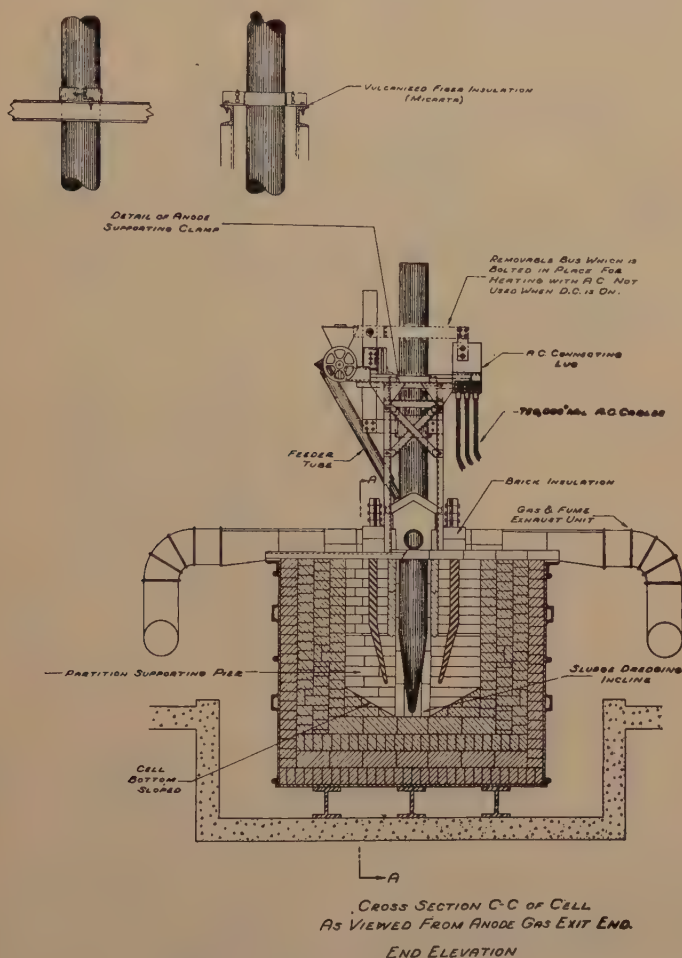
LONGITUDINAL SECTION A-A OF CELL
SECTION THRU SLUDGE DREDGING WELL
FRONT ELEVATION OF SUPERSTRUCTURE

FIG. 2.—DETAILS OF 8000-AMPERE PILOT CELL.

END ELEVATION B-B OF CELL

The steeply sloping end was provided on the anode chamber to facilitate the removal of accumulated sludge from under the anodes. It did not serve the purpose

sampling tube attached to the anode enclosures provided for collection of gas samples for analysis, and a duct at the end of the chamber was attached to an exhaust



LEGEND



DENSE FLINT ACID PROOF BRICK



DENSE LIGHT BURNT FLINT BRICK



COMMON BRICK

FIG. 2.—SEE OPPOSITE PAGE FOR DESCRIPTIVE LEGEND.

very well and later was filled in. An enclosure around the anodes, supported on the compartment partitions, confined the anode gases and prevented excessive oxidation of the anodes by air. A gas-

fan for control of gaseous products of decomposition.

Six graphite or carbon anodes, 8 in. in diameter, were suspended from the supporting superstructure. Each anode was

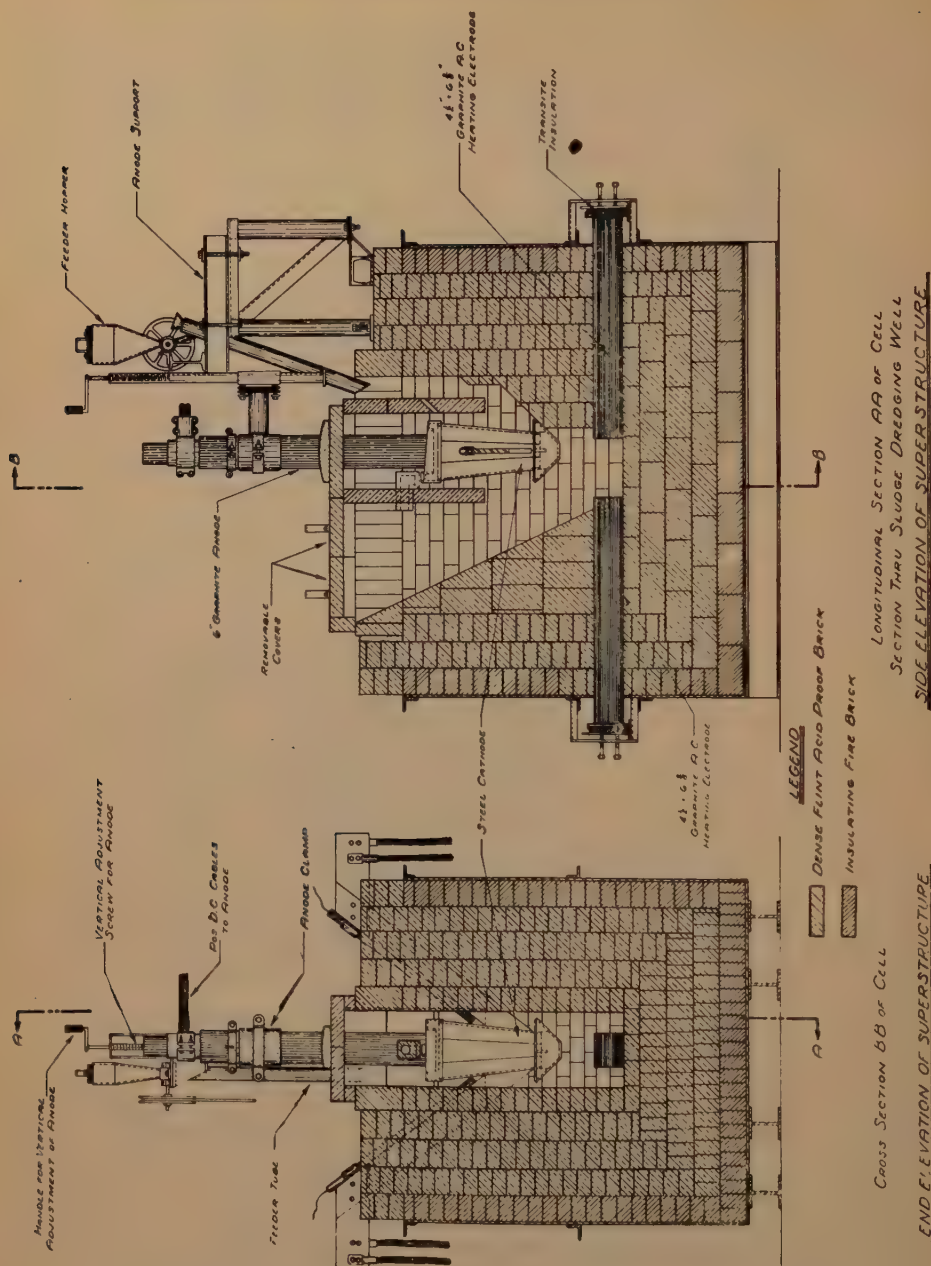


FIG. 3.—TEST CELL, USING NEW CELL DESIGN.

connected individually to the positive bus bar by heavy cast copper clamps and connecting buses. The depth of immersion in the bath was adjusted by releasing the

under surface to prevent attack by the cell gases. Exhaust ducts, connected to a 5000-cu. ft. per min. blower, were placed beneath the working floor along the side

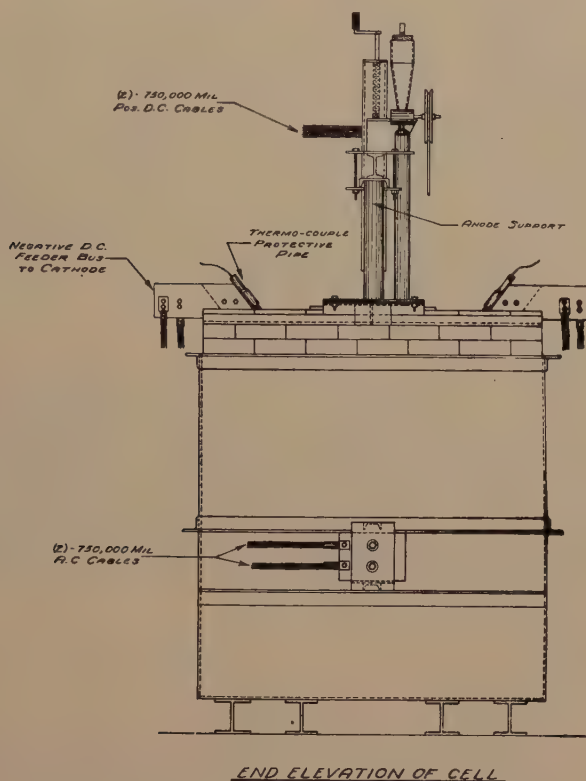


FIG. 3.—SEE OPPOSITE PAGE FOR DESCRIPTIVE LEGEND.

clamps and raising or lowering the electrode by an overhead monorail hoist.

The cathodes, three on each side of the cell, were iron and steel members individually cast to the shape shown in Fig. 2. The bottom flattened section was inclined toward the anode to correspond roughly to the taper assumed by the anodes. These cathodes were replaced eventually by rolled steel cathodes of various shapes, to permit studying the effects of cathode shape on cell operation. The cathode chambers also were enclosed by removable steel covers, to restrict infiltration of air. Radiation from the top surface of these covers kept the steel cool enough on the

of the cathode chamber on each side of the cell. The ventilator system was used to exhaust gaseous products when the cathode or anode chambers were open. Power for electrolysis was supplied by 40 copper oxide rectifier units connected in series-parallel to deliver 0 to 10,000 amp. at 0 to 12 volts.

The test cell shown in Fig. 3 was one of many small cells built to determine the effects of specific impurities. Some of these had bottom anodes and other radical modifications. The cell shown was the final result of these tests. The anode and cathode are placed concentrically to reduce voltage drop and to cause an upward circulation of

bath between the anode and cathode. The cathode is provided with eight ribs on the inner surface to provide certain areas of high cathodic current density. The cell feed is added continually to a separate feed chamber, where it is gradually wetted by the bath and sinks into the compartment at the bottom of the anode. The metal rises and is forced into the relatively calm area outside the brick partition where it can be periodically removed. The inverted trough shown in Fig. 3, over the cathode, was found to be unnecessary and was removed. The metal then rose to the surface and was forced out through a hole in the partition. The bath level normally was kept slightly higher than the top of the hole. No steel surfaces extended above the bath level, where they could be acted upon by the cell gases or by the atmosphere to cause contamination of the bath by iron.

A new 10,000-amp. pilot cell was designed to embody the features shown in the test cell (Fig. 3). Fig. 4 shows this cell under construction. Operating data from this new pilot cell are not yet available.

THE RAW MATERIALS

Anhydrous magnesium chloride for initial electrolyte make-up was obtained from three commercial sources. The analyses of these materials are shown in Table 1.

Magnesia for use as cell feed, or for the preparation of cell feed, was obtained from many sources. The major portion was produced from Sloan dolomite,³ with minor quantities from a Washington magnesite and a Pennsylvania dolomite. Magnesia was also obtained from several available commercial sources, but it was found that none of these was sufficiently pure to give satisfactory cell operations. Analyses of the magnesia used for cell feed are shown in Table 2.

At the beginning of the investigation the magnesia was added to the bath directly and losses of MgCl_2 were made up

with anhydrous magnesium chloride from a commercial source. As work progressed it became obvious that some of the MgCl_2 would always be lost by electrolysis and removal of sludge as well as by minor losses such as volatilization, hydrolysis, and oxidation. To make up for these losses during operations of the pilot cell, the pulverized magnesia was mixed with pulverized coke or other carbon and treated with chlorine at temperatures between 525° and 575°C . This operation was carried out on a continuous basis in a small, externally heated rotary kiln fitted with a ceramic lining. Ordinarily about 15 per cent of the magnesia was chlorinated.

TABLE 1.—Analyses of Magnesium Chloride Used for Initial Electrolyte Make-up
PER CENT

Component	Sources		
	A	B	C
MgCl_2	93.00	95.60	92.10
CaCl_2	1.69	1.69	3.47
KCl	0.99	0.84	2.16
NaCl	1.28	1.27	1.95
H_2O insol. (mostly MgO)..	3.04	0.80	0.32

Subsequently a pilot plant was constructed and operated for the production of a high-purity magnesia containing sufficient magnesium chloride to make up all cell losses. This product was specifically produced for the process by the controlled

TABLE 2.—Analyses of Magnesia Used for Cell Feed
PER CENT

Source	CaO	Fe_2O_3	Al_2O_3	SiO_2	SO_4	B_2O_3
Sloan dolomite.....	1.80	0.36	0.04	0.08	0.34	0.003
Washington magnesite.....	1.89	0.65		0.82	0.90	
Luning magnesite.....	2.66	0.89	0.10	1.44	0.35	0.010
Sea water, source D.....	1.13	0.21	0.18	1.02	0.64	0.330
Source E.....	1.29	0.27	0.13	1.40	1.05	0.062
U. S. P. MgO	1.01	0.07	0.07	0.35	0.45	0.010
Pennsylvania dolomite ^a	3.31			0.92	2.33	0.003

^a Initial 400-lb. batch.

hydrolysis and dehydration of magnesium chloride hydrates prepared from Pennsylvania dolomite. An analysis of this special cell feed is shown in Table 3. It should be

Boulder City Experiment Station. Supplementary research was performed at the Intermountain Experiment Station, Salt Lake City, where determinations were



FIG. 4.—PILOT CELL OF NEW DESIGN UNDER CONSTRUCTION.

noted that 30 per cent MgCl_2 actually represents only 16 per cent of the total magnesium content of the feed.

TABLE 3.—*Composition of Cell Feed*

MATERIAL	WEIGHT, PER CENT
MgO	66.0
MgCl_2	30.0
CaCl_2	Not over 2.0
Fe_2O_3	Not over 0.02
SiO_2	Not over 0.02
B_2O_3	Not over 0.005
SO_4	Not over 0.10
H_2O	Not over 2.00

OPERATIONS

The oxide electrolysis process has been developed through various stages of laboratory, small-scale cell, and pilot-cell demonstration work. Because of the urgency of wartime needs and the desire to perfect a commercial process as soon as possible, the sequence of operations did not always follow the most logical line of development. Original small-scale tests and all pilot-plant work were performed at the

made of the relationships existing in the system $\text{MgO-B}_2\text{O}_3\text{-MgCl}_2$, as well as studies on the effects of other alkali and alkaline earth chlorides and the conductivity and density of various mixtures of chlorides. These studies were helpful in the interpretation of the results obtained in the pilot cell.

A series of tests, each of several days duration, was conducted using the cell shown in Fig. 1. The bath consisted of fused magnesium chloride, containing essentially no other chlorides, and was maintained at $815^\circ\text{C.} \pm 10^\circ\text{C.}$ The gases produced in the cell were collected and scrubbed with an alkaline $\text{Na}_2\text{S}_2\text{O}_3$ solution in an absorption tower, to determine the quantity of chlorine evolved during electrolysis. Boric oxide was added to the melt to give 0.3 per cent B_2O_3 at the start of the campaign, and more was added from time to time to maintain the concentration in

the cell at about 0.15 per cent. The magnesium oxide, U.S.P. grade, was added at hourly intervals.

This preliminary test work showed that by feeding the cell with an excess of magnesium oxide above the quantity required for metal production, no chlorine at all was produced during a 10-day campaign, although some HCl was always present in the anode gases. The excess oxide added, however, eventually segregated as sludge in the bottom of the cell and finally disrupted effective operations by covering the openings between the anode and cathode compartments. This sludge consisted principally of $MgCl_2$ mixed with MgO , and its removal from the cell resulted in a high loss of $MgCl_2$. From the results of these tests it was concluded that the net loss of magnesium chloride would be lower if less MgO was maintained in the electrolyte, even though this resulted in some loss of chlorine at the anode.

During a subsequent test of 384-hr. duration, the MgO was added carefully by manual feeding at 15-min. intervals in just sufficient quantity to maintain the chlorine in the anode gases within 1 or 2 per cent. Good operating conditions were attained during this test and little difficulty was experienced from accumulation of sludge. A material balance is shown in Table 4.

The results of this preliminary work were considered satisfactory enough to warrant additional development work on a pilot scale and the cell shown in Fig. 2 was constructed for this purpose. More than 10 tons of magnesium were produced in this cell during the course of 27 campaigns. The campaigns varied in length from a few days to several weeks, each serving to test a particular bath composition, cathode arrangement, anode position, type of anode (graphite or carbon), method of operation, or cell feed. The first 11 campaigns, and part of campaign 12, were conducted using cell feed prepared from Sloan dolomite. Some difficulty was experienced at times

from metal dispersion, with resultant loss of current efficiency, but campaigns 7, 8, 9, 10, 11 and 12 were fairly successful. After the pilot-plant operations with Sloan dolomite ceased, caustic-calcined magnesia (source D, Table 2) was purchased from a commercial producer. This material caused such severe metal dispersion that continuous operations were practically impossible. Tests were also made using magnesia from other sources, but they all contained too many impurities for successful operations. Campaign 12, in the pilot cell, lasted for 47 days and covered a period when the cell feed was prepared from Sloan dolomite and a period when sea-water magnesia (source D) was used. It has been selected for more detailed discussion.

TABLE 4.—*Material Balance for Small-scale Test*

	POUNDS
MgO	
MgO added.....	142.3
MgO removed in sludge (33 per cent of sludge).....	6.1
MgO available for cell reactions.....	136.2
Magnesium in available MgO.....	82.5
MgCl₂	
MgCl ₂ added.....	160.1
MgCl ₂ absorbed in lining and removed in sludge (bricks in lining were removed, weighed, sampled and analyzed).....	84.0
MgCl ₂ available for cell reactions.....	76.1
Magnesium in available MgCl ₂	19.0
Magnesium	
Magnesium available in MgO.....	82.5
Magnesium available in MgCl ₂	19.0
Total magnesium available.....	101.5
Magnesium produced.....	95.2
Unaccounted for.....	6.3
Additional Data	
Carbon consumed, lb.....	30.7
Lb. carbon per lb. magnesium.....	0.32
Lb. sludge per lb. metal.....	0.2
Average ampere efficiency, per cent.....	70.0

Campaign 12 in the Pilot Cell

Campaign 12 was characterized by a relatively low $MgCl_2$ electrolyte. The low $MgCl_2$ content made suppression of chlorine difficult and for this reason sludge formation was higher than for some previous campaigns. This was offset somewhat by lower consumption of anodes.

The chlorinated magnesia used for cell feed was mixed with pulverized low-ash coke in 700 to 800-lb. batches and added to the hoppers of the continuous feeders

at $\frac{1}{2}$ -hr. intervals. The feeders fed continuously to the cell where the material immediately sank. It did not float on the bath. The proper quantities of MgO and

Table 5 shows the variations of cell potential and current efficiency (metal recovery) from day to day. The cell potential was never constant. This phe-

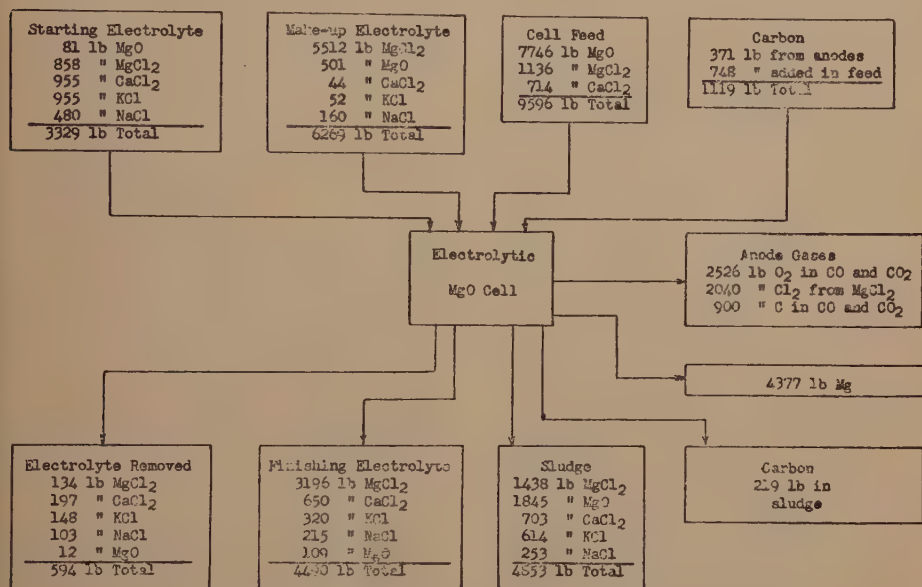


FIG. 5.—MATERIAL BALANCE FOR CAMPAIGN 12.

carbon required by the cell were determined by the analysis of the anode gas. Gas analyses were run at hourly intervals, and each batch of cell feed was carefully sampled and analyzed. Samples of the electrolyte were taken under the surface of the bath in the cathode chamber at least once each shift and analyzed for MgCl₂, KCl, NaCl, CaCl₂, MgO, and carbon. The metal was removed from the cathode chambers at 24-hr. intervals by dipping with steel ladles.

The sludge was removed from the back of the cathodes at 48 to 72-hr. intervals. At these times several pounds of metal rose from the sludge and were added to the day's production. The sludge was cooled, pulverized, sampled and analyzed. The sludge normally analyzed between 37 and 40 per cent MgO. Part of this (3 to 4 per cent) was actually present as magnesium metal.

nomenon was found to be caused by a changing anode potential and a partial shorting out of cell current by a conductive layer in the cell bottom. In some cases experimental changes in the anodes or cathodes were responsible for the fluctuations in voltage. The cell feed was changed on the twenty-sixth day and the current efficiency dropped steadily from that time because of dispersion of metal at the cathode.

A complete material balance for the campaign is shown in Fig. 5. The compositions of the electrolyte at the start and finish do not agree with the MgCl₂ analyses shown in Table 5. The explanation of this is that the MgCl₂ content of the starting electrolyte was so low that satisfactory operations could not be obtained. Hence, some of the electrolyte was removed and the MgCl₂ content was made up to the

56.5 per cent shown in Table 5; at the end of the campaign the bath level was low and make-up electrolyte was used to raise the bath level to a point that had been calibrated originally. This raised the

TABLE 5.—*Current Efficiency and Cell-potential Variations*

Duration of Campaign, Days	Current Efficiency, Per Cent	Cell Voltage	Average Amperes	MgCl ₂ Content of Electrolyte
1	38	9.3	6830	
2	20	9.8	7030	56.5
3	54	8.8	7430	56.0
4	65	8.6	8160	57.5
5		9.3	7930	54.5
6	55.1	8.6	7300	55.6
7	72	8.9	7230	55.9
8	85	9.1	6770	54.8
9	62	9.6	7200	54.5
10	80	8.7	6900	51.3
11	66	9.4	6560	53.4
12	60	9.2	6380	51.9
13	60	9.0	6440	51.9
14	31	9.1	6480	52.2
15		9.3	5310	59.5
16	69	10.3	6100	54.1
17	74	10.6	7180	53.5
18	75	11.6	6020	50.4
19	64	10.6	6700	50.1
20	64	10.5	6850	59.5
21	61	10.7	7040	55.7
22	70	10.7	6550	56.8
23	61	10.6	7110	57.5
24	70	9.9	6840	54.4
25	61	9.9	6225	56.1
26	70	10.0	7090	53.8
27	62	9.5	6210	56.3
28	49	9.9	6300	57.4
29	60	9.4	6275	55.9
30	51	10.0	6350	55.6
31	49	10.3	6100	54.7
32	58	10.6	5840	53.7
33	53	10.7	6300	54.5
34	45	10.2	5920	54.9
35	63	10.0	5720	54.6
36	49	10.1	5960	55.7
37	54	9.7	6250	53.9
38	50	9.2	5940	54.7
39	43	9.2	5192	53.8
40	37	8.5	5910	54.9
41	43	8.5	6441	54.6
42	36	8.8	6100	53.4
43	40	9.3	6070	54.2
44	36	9.3	5870	52.5
45	31	8.8	6530	50.2
46	20	7.8	6330	50.4
47		9.4		49.3

MgCl₂ content to 71.18 per cent, as in Fig. 5. A recapitulation of the magnesium balance is shown in Table 6.

Special Tests

It was decided that pilot-cell work should be recessed until a plant could be constructed and operated for producing ade-

quate quantities of high-purity magnesia for cell feed. During this period special tests were carried out in a variety of cells in an effort to determine the effects of individual impurities and the maximum

TABLE 6.—*Material Balance of Campaign 12 Showing Source of Magnesium Produced*

	Con-stituent, Per Cent	Weight Lb.
Balance on the magnesium oxide		
MgO in the starting electrolyte.	2.41	81
MgO in the make-up electrolyte.	7.99	501
MgO in the cell feed.....	80.72	7746
Total MgO added.....		8328
MgO in electrolyte removed to change bath analysis.....	2.02	12
MgO in electrolyte at end of campaign.....	2.43	109
MgO in sludge.....	38.01	1845
Total MgO removed.....		1966
MgO available for cell reactions, 8328 - 1966.....		6362
Magnesium equivalent to MgO.		3836
Balance on the magnesium chloride		
MgCl ₂ in the starting electrolyte	25.77	858
MgCl ₂ in make-up electrolyte...	87.92	5512
MgCl ₂ in the cell feed.....	11.84	1136
Total MgCl ₂ added.....		7506
MgCl ₂ in the electrolyte removed to change bath analysis	22.55	134
MgCl ₂ in electrolyte at end of campaign.....	71.18	3196
MgCl ₂ in sludge.....	29.63	1438
Total MgCl ₂ removed.....		4768
MgCl ₂ available for cell reactions, 7506 - 4768.....		2738
Magnesium equivalent to MgCl ₂		698
Balance on the magnesium metal		
Total magnesium from MgO and MgCl ₂ , 3836 + 698.....		4534
Actual Magnesium produced....		4377
Magnesium unaccounted for..		157
Proportion of metal obtained from MgO.....	84.6	
Proportion of metal obtained from MgCl ₂	15.4	

allowable concentration of critical impurities in the cell feed. The new cell design shown in Fig. 3 was developed during this period. The conclusions arrived at from this work in relation to impurities as well as other variables are treated in the following section.

GENERAL TECHNICAL DISCUSSION

To develop logically a reasonable explanation for the observed facts the system under consideration will be synthesized from its elements and step by step the possible effects of added components will be deduced. Therefore, the initial premise involves the assumption that only pure components are present or added.

During the course of this discussion, allusion will be made to certain terms that are defined as follows:

1. The equilibrium reaction potential is the theoretical value based on the free energy of the process under consideration.

2. The decomposition potential is the minimum potential (excluding the internal resistance drop) required for continuous electrolysis.

3. The term "polarization" includes all departures of the potential during electrolysis from the equilibrium reaction potential. It may vary with the current density and is equal to the difference between the equilibrium potential for the specified electrode reaction and the dynamic potential (that is, the potential when current is flowing, excluding IR drop). It is a measure of irreversibility.

4. Overvoltage is the minimum polarization required for continuous electrolysis at an appreciable rate under given conditions on any specified electrode. It equals the difference between the equilibrium and the decomposition potentials.

5. The bath voltage is the total voltage between the anode and the cathode of an electrolytic cell during electrolysis. It is equal to the sum of: (a) equilibrium reaction potential; (b) IR drop; (c) anode polarization; (d) cathode polarization. It is the value ordinarily measured with the potentiometer or voltmeter during electrolysis.⁴

6. Current efficiency is the ratio of the theoretical quantity of electricity to that actually used for the separation of a definite amount of substance.

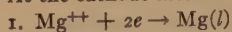
To avoid confusion, the system in each case will be considered as made up of three regions—the anode-melt interface, the cathode-melt interface and the body of the bath. It is not possible to make an exact specification as to the extension of the electrode interface zone into the body of the melt, since there is a moot question as to the effect in the system under consideration of chemical reactions involving chlorine, say at a distance of several millimeters from the anode, upon the vapor pressure of chlorine being discharged at the anode, and thus upon the equilibrium reaction potential.

The primary system to be set up is composed of a fused bath at 800°C containing 99.5 wt. per cent of MgCl_2 and 0.5 per cent MgO in solution in the MgCl_2 .⁵ The cathode material is steel, while the anode is graphite. In such a system it is supposed that dissociation is complete, the process of fusion merely breaking down the solid into its pre-existing ions. While this point may be controverted, at any rate there must be present charged particles to carry current, since Faraday's laws of electrolysis are strictly applicable to the system.⁶

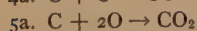
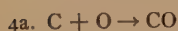
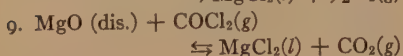
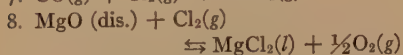
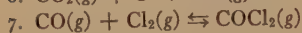
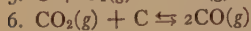
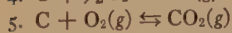
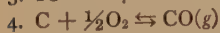
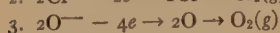
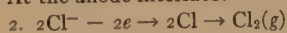
When an increasing external electromotive force is impressed upon the system, ions of proper charge sign migrate to the region of the electrodes until the impressed voltage is sufficient to overcome all resistances, such as IR drop and polarization factors, and in addition to provide sufficient energy for the metal ion to gain electrons and be discharged in molecular form at the cathode, and the anion to lose an electron and be discharged at the anode. Upon discharge of anion and cation, secondary chemical reactions may take place either with the electrode material or with bath constituents that may modify the decomposition voltage.

The reactions possible in the primary systems are: MgO (dis.) representing MgO in solution in MgCl_2 :

a. At the cathode interface:

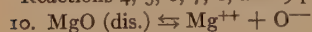


b. At the anode interface:



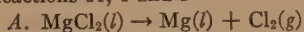
c. In the body of the melt:

Reactions 4, 5, 6, 7, 8, and 9 plus

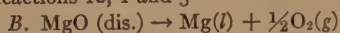


These reactions may combine, or occur simultaneously, to produce the following summation reactions:

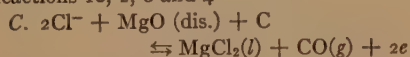
Reactions 11, 1 and 2



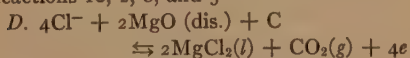
Reactions 10, 1 and 3



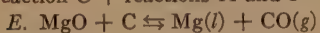
Reactions 10, 2, 8 and 4



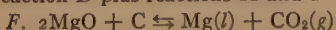
Reactions 10, 2, 8, and 5



Reaction C + reactions 11 and 1



Reaction D plus reactions 11 and 1



Following are the equilibrium reaction potentials, in volts, for reactions A, B, E, and F at 800°C.:

Reaction	E°	Reaction	E°
A	2.460	E	1.459
B	2.520	F	1.486

All these values were calculated from free-energy equations developed by K. K. Kelley in the forthcoming Bureau of

Mines *Technical Paper* 676: Energy Requirements and Equilibria in the Dehydration, Hydrolysis and Decomposition of Magnesium Chloride. In these calculations, in reactions involving MgO, the solution is assumed to be saturated with no free-energy change between solid MgO and MgO (dis.).

On the basis of the thermodynamic considerations detailed above, coupled with certain kinetic data, the reaction mechanism can be postulated by first making certain idealizing assumptions. Assuming that the anode and cathode are only far enough apart to permit insertion of an ideal membrane, permeable to both anions and cations but not to gases or liquid metal, the IR drop is the minimum possible. Under these conditions, the bath voltage, for all practical purposes, will be equivalent to the sum of the equilibrium reaction potential, the anode polarization and the cathode polarization.

When an external electromotive force is impressed on the system, there is a migration of Mg^{++} ions to the vicinity of cathode and of Cl^- , and O^{--} ions, if present, to the anode. Had the bath been composed only of MgCl_2 it would be necessary to impress an e.m.f. of 2.49⁷ volts before continuous electrolysis could take place. However, since MgO is present in solution, the chlorine vapor pressure is reduced through interaction between MgO, chlorine and the carbon anode, so that electrolysis can take place at a much lower voltage than 2.49. The average for six small-scale tests at 800°C. was found to be 1.76 volts,⁸ determined by extrapolation to zero current. It is to be expected that this value would be higher than the calculated 1.46 volts for the summation reaction of lowest value because the equilibrium vapor pressure is difficult to obtain. If the observed depolarization of the anode is considered to be caused entirely by a decrease in chlorine vapor pressure, the vapor pressure at zero current, corre-

sponding to 1.76 volts, would be about 1×10^{-6} atmospheres.

One might expect that the off gases of the cell would contain a high proportion of CO compared to CO₂, in view of the work of Pidgeon and Phillips on the kinetics of the production of anhydrous MgCl₂.⁹ It is stated therein that the reaction between MgO, C and Cl₂ results in the off gas containing 100 per cent CO at temperatures above 900°C. and 88 per cent at 800°C. However, no gas analyses were given in this paper.

In the operation of the several cells under discussion the ratio of CO₂ to CO was of the order of 10:1 or greater. Kinetic studies on a typical electrolyte, containing MgO and carbon, showed that while the rate of MgCl₂ formation on passage of Cl₂ at 800°C. was somewhat slow the off gases under the best conditions contained 76.5 per cent CO₂ as compared with 17.1 per cent CO. The CO ratio was increased by a large excess of carbon. Attention is also called to the work of Stover and Constantinescu on the system Al₂O₃-C-Cl₂ who found little, if any CO in their off gases.¹⁰

In view of this discussion, it is therefore postulated that the major reaction mechanism in the simple system is that MgCl₂ is electrolyzed, the MgO present reacting with chlorine and carbon at the anode interface to form MgCl₂ and in the main CO₂. This means that summation reaction F largely predominates over the summation reaction E.

The production of Mg (l) at the cathode introduces the first complication in the primary system, since it has a certain solubility in the melt, thus making the system to be dealt with MgO (dis.)-MgCl₂(l)-Mg(l). The equilibrium solubility of Mg(l) in pure MgCl₂(l) has been determined as approximately 0.6 per cent at 750°C. and 0.4 per cent at 870°C.¹¹ The difficulties engendered by this have been discussed by Drossbach,¹² who states:

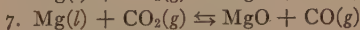
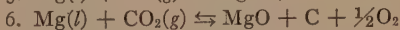
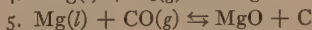
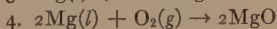
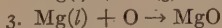
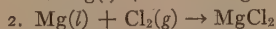
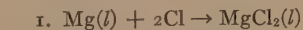
At the cathode, a part of the discharged metal goes into suspension as metal fog, the quantity depending on the magnitude of its solubility, its rate of solution, and the degree of circulation of the electrolyte. The metal fog thus formed migrates to the anode due to the circulation of the electrolyte (kept at constant temperature), brought about by the evolution of gases at the anode. A part of this metal that has gone into suspension or solution reacts even at some distance away from the anode with the anode gases, or a part of this metal fog may reach air-exposed surfaces of the electrolyte and there oxidize, in either case giving rise to irreversible current efficiency losses. The remainder of the metal fog reaches the surface of the anode and, as a consequence of the interaction between the metal fog and the anode gases, reduction in concentration of the anode gases takes place, resulting in a depolarization of the anode. If this depolarization takes place very rapidly then the process is reversible.

The possible reactions due to formation of metal fog are:

a. At the cathode:

None

b. At the anode:



c. In the body of the melt:

Same as above, with exception of 1 and 3

Effect of Materials Added to System

*Addition of KCl, NaCl and CaCl₂.—*A pure magnesium chloride electrolyte is neither commercially feasible nor desirable and, except for original small-scale tests, the electrolytes always consisted of MgCl₂ with CaCl₂, NaCl, and KCl. In some cases a small quantity of CaF₂ was added. It is expedient to add alkali and alkaline earth chlorides to increase the conductivity of

the electrolyte, to decrease its melting point, and to minimize losses of MgCl_2 through sludge "drag out." Varying amounts of calcium chloride are always

and wetting property, but more effect on specific gravity.

In the first pilot cell (Fig. 2), the MgCl_2 concentration in the electrolyte had a

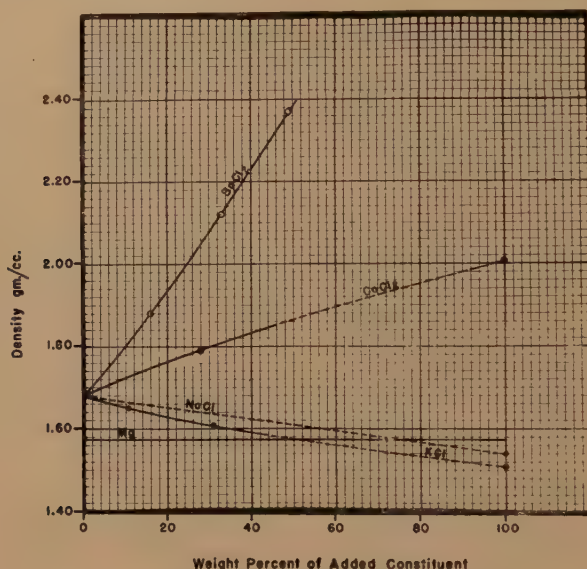


FIG. 6.—EFFECT OF ADDED CHLORIDES ON DENSITY OF BATH.

present, since it is impractical to eliminate this material from the cell feed, while the NaCl and KCl are added as anhydrous salts. Density and conductivity curves given in Figs. 6 and 7, from determinations made by Potter and Huber,¹³ show the effects of adding these chlorides to magnesium chloride baths at 800°C .

Another effect of the added chlorides is decreased "wetting" property of the electrolyte—the property necessary to prevent burning of magnesium on the surface of the bath—which is a factor of particular importance when operating at 800°C . Sodium chloride rapidly decreases this wetting property and concentrations greater than 25 per cent could not be readily used. Fortunately the increase in conductivity by the addition of NaCl is most rapid at concentrations below 20 per cent. Potassium chloride has less effect than sodium chloride both on conductivity

marked effect on the proportion of carbon consumed from the anodes and that consumed from the bath, the latter being added as finely divided carbon with the feed. During campaign 7, when the electrolyte averaged 83.5 per cent MgCl_2 , a total of 609 lb. of carbon was consumed, of which 79 per cent came from the anodes and 21 per cent from the feed. In campaign 12, the electrolyte averaged 55 per cent MgCl_2 , and of the 1119 lb. of carbon consumed 33 per cent came from the anodes and 67 per cent from the feed. Total carbon consumption was 0.26 lb. per pound of metal in both cases. In general, when the MgCl_2 concentration was below 50 per cent practically no anode carbon was consumed and when the MgCl_2 concentration was 90 per cent no suspended carbon was consumed. Chlorine control was very difficult when the electrolyte contained less than 55 per cent MgCl_2

and 60 to 65 per cent was more satisfactory from this viewpoint.

Thus, a satisfactory bath composition consists of about 65 per cent MgCl_2 ,

of the melt takes place between MgO in solution, diffused chlorine and carbon.

Consider individual particles of solid MgO and carbon, in suspension in a bath

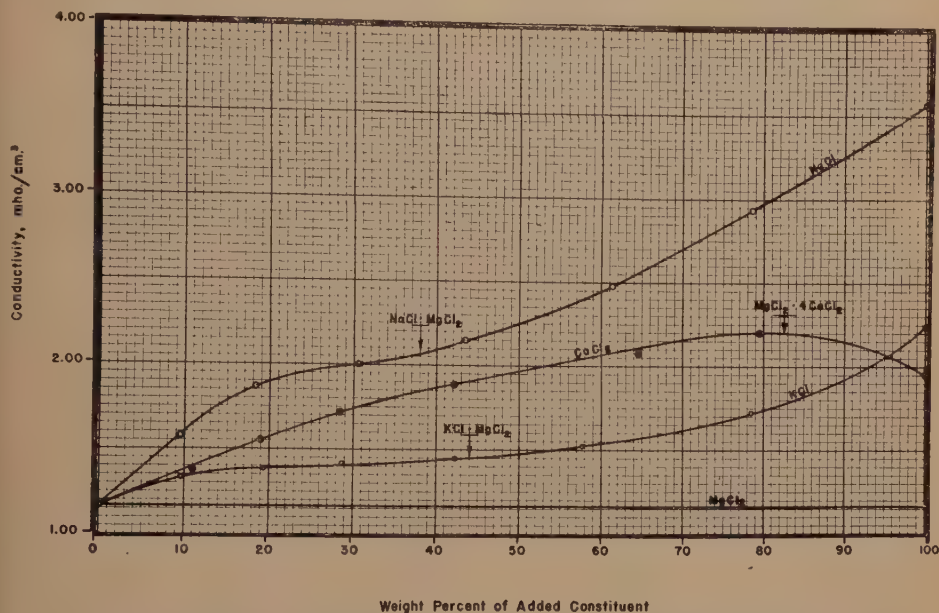


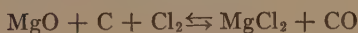
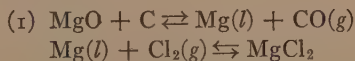
FIG. 7.—EFFECT OF ADDED CHLORIDES ON ELECTRICAL CONDUCTIVITY OF BATH.

20 per cent NaCl , and 15 per cent CaCl_2 . In the operation of the pilot cell the CaCl_2 concentration was maintained by balancing the input in the cell feed with removals as a sludge constituent, and when a MgCl_2 concentration of less than 65 per cent was used KCl was added, to supplement the NaCl or replace part of it.

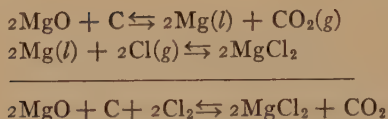
It is believed that the carbon consumption phenomenon accompanying decreased MgCl_2 concentration is caused by decreasing utilization of chlorine at the anode interface and increasing utilization by reaction between MgO and C suspended in the bath with chlorine that diffuses from the anode into the melt. Chlorine diffusion apparently was increased with decreasing MgCl_2 concentration.

Basing the argument chiefly on probability, it can be postulated that this secondary chemical reaction in the body

of molten MgCl_2 and other chlorides. Each particle (depending on its rate of movement through the bath) will be surrounded by a stationary film of molten chlorides of unknown but definite thickness. If both materials are insoluble, the reaction, no matter what the steps involved, between MgO , Cl_2 , and C , will be dependent on a collision between the particles and their getting into such a proximity despite the intervening films, that interionic forces can come into play. As shown by the calculations of Kelley,¹⁴ the likelihood that the steps involved in the reactions are:

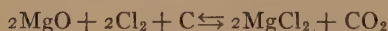
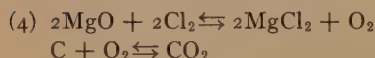
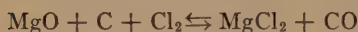
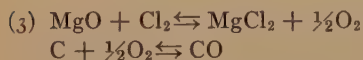


or (2)



is extremely slight, since the free-energy change for the primary reaction in each case at 1100°K. is $\Delta F^\circ = 65, 270$ and 135, 790, respectively.

That the steps involved are:



(r (5)

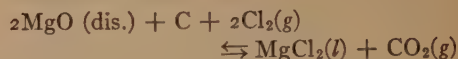
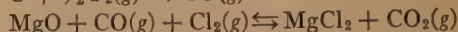
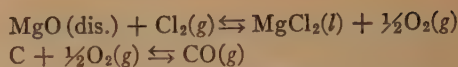


are more likely based on thermodynamic considerations, since Kelley has shown that the ΔF° at 1100°K. for the primary reaction in each case ($\text{MgO} + \text{Cl}_2 \rightleftharpoons \text{MgCl}_2 + \frac{1}{2}\text{O}_2$) is 2660 and

$$K = \frac{P \cdot \frac{1}{2}\text{O}_2}{P \cdot \text{Cl}_2} = 2.81 \times 10^{-1}$$

The rate and extent of this reaction will be governed by the rate of diffusion of Cl_2 and O_2 through the film of MgCl_2 on an MgO particle in opposite directions, and the rate of diffusion of O_2 , and/or CO and CO_2 through the film of MgCl_2 surrounding a carbon particle that *must be in close proximity to the MgO particle.* The equilibrium solubilities of the several gases in MgCl_2 will have an important bearing on the rate and extent of the over-all reaction.

It is felt that increased probability is involved in the stipulation that the reaction mechanism is



since in this instance the only diffusional resistances involved are those of Cl_2 and CO_2 in opposite directions through a film of MgO (dissolved in MgCl_2) surrounding a carbon particle. It is also probable that with the dissolved MgO a compound is formed between MgO and MgCl_2 .

Water.—Owing to the hygroscopic nature of MgCl_2 and its lower hydrates, it is impossible to avoid introducing a certain amount of water into the bath with the feed, since this material always contains MgCl_2 as well as MgO .

The primary effect of the water is to decompose some MgCl_2 into MgO and HCl , as shown by the cell-gas analyses, but some of the water remains in solution and is decomposed by the electrochemical reaction:



Although it may be difficult to conceive of this event as taking place in a molten bath at 800°C., Seyl and Thompson¹⁵ have shown that the low results of previous workers on the decomposition potential of Al_2O_3 in cryolite baths can be ascribed to the fact that the bath was not electrolyzed long enough to eliminate water and that the potential found, 1.23 volts, is that of water. This factor must be considered, since in this system water is being continuously introduced with the feed.

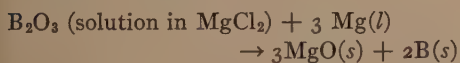
It is probable that water in the electrolyte has other effects but no other specific effects were caused by the small quantity of water introduced with the feed.

Magnesium Oxide.—The magnesium oxide introduced into the cell or formed by the hydrolysis and decomposition reaction

could and did at times act as an impurity. By some means the small particles acted as positively charged colloidal particles and plated out in a dense, adherent layer that sometimes attained a thickness of more than $\frac{1}{2}$ in. on the cathode. The MgO could have acquired a positive charge by absorption of positively charged ions. This phenomenon was most noticeable when certain other impurities, particularly sulphates, were present in the bath. Such plating of oxide along with impurities in the electrolyte was a major cause of sludge formation in the cell. In other words, an appreciable proportion of the cell sludge first accumulated on the bottom of the cathodes and then slid off into the cell bottom.

Boric Oxide and Borates.—As described in the introduction, the initial work on this process was based on the fact that in the presence of B_2O_3 , MgCl_2 would dissolve appreciable quantities of MgO . However, it was discovered that on continuous electrolysis over long periods the presence of B_2O_3 had a highly detrimental effect because of its reaction with Mg globules at the cathode, causing dispersion of the metal and loss of current efficiency.

It was shown in the solubility studies referred to in preceding paragraphs that B_2O_3 is completely reduced in the presence of $\text{Mg}(l)$, the reaction being



Chemical and spectrographic analyses showed that the solubility of boron in liquid magnesium was less than 0.01 per cent. It was likewise found that B_2O_3 would also react with chlorine in the vicinity of the anode and be volatilized as BCl_3 . In the cell tests, it was found that in addition to the reactions noted above, B_2O_3 tended to disappear from the bath as an ingredient of the sludge.

During initial operations, while B_2O_3 or borate was being added to the bath,

it was noted that it had an immediate effect on the lowering of the decomposition voltage and on the suppression of chlorine evolution. However, the effect gradually wore off until at the end of several days it again became necessary to add boron as either B_2O_3 or $\text{Na}_2\text{B}_4\text{O}_7$.

Could it have been possible to confine the activity of the B_2O_3 to the vicinity of the anode, it might well have been a most useful addition agent, since it, or rather BCl_3 , is a well-known homogeneous catalyst for chlorination reactions, and probably it played that role at this point. However, its reaction with metal at the cathode not only caused irreversible current-efficiency losses but had an effect that, in course of time, resulted in the formation of a tough, viscous sludge on the cell bottom, which contained enough metallic magnesium to render it highly conductive and thus shunt current directly between the electrodes. In extreme cases, the metal recovery dropped to zero. The exact cause of this latter phenomenon is unknown, unless it can be ascribed to the formation of a layer of boron and MgO on the surface of small globules of Mg as they are formed at the cathode, thus preventing their coalescence and permitting their settling to the bottom of the bath.

As appreciable amounts of current were carried through the conductive sludge layer there were times when the cell-bottom temperature exceeded 900°C . When this happened, owing to the volatility of $\text{Mg}(l)$, the Mg content of the bath increased, with results described above under the reference to the work of Drossbach. The combined effect of boric oxide causing metal to drop from the cathode into the sludge and the reaction between metal dissolved in the bath with chlorine at the anode was to cause a drop of metal production to zero.

Iron.—There is little likelihood that iron exists in appreciable quantities in the bath as FeCl_3 . Its vapor pressure in the

pure state is one atmosphere at approximately 300°C. and, despite the marked lowering of its vapor pressure in molten NaCl,¹⁶ its existence per se at 800°C. must be limited. This assumption is borne out by the fact that an attempt to purge iron from one of the baths by bubbling chlorine through it caused copious evolution of FeCl₃ fumes for a time. However, continued chlorine input did not appear to affect a certain amount of residual oxide that remained in the bath. A reason for this may be the exceedingly slow rate of solution of iron oxides, particularly Fe₃O₄ in the melt.

As demonstrated by the test outlined below, there is obviously an interrelationship between B₂O₃ and iron in the bath as far as detrimental effects go. For this test a round-pointed steel cathode, 3 in. in diameter, was used in a bath consisting of 80 per cent MgCl₂, 13 per cent CaCl₂, and 7 per cent alkali chlorides. The anode and cathode compartments were separated by a ceramic louvered partition, and the cathode was placed about 4 in. back of this partition in a quiescent pool, where the plating action could be observed. After several days of operation, the iron in the electrolyte was reduced to values ranging from 0.01 to 0.05 per cent Fe₂O₃. Enough Na₂B₄O₇ was added to make 0.03 per cent B₂O₃ in the bath. Metal production decreased until at the end of four days no metal was being produced. Observation of the cathode showed that small balls of magnesium collected on the cathode surface and, after reaching a diameter averaging 1/8 in., rolled down and dropped off the tip. Since virtually no anode gas was being produced, it was obvious that the metal was recombining as rapidly as it was formed. At that time an analysis of the electrolyte showed 0.45 per cent water-insoluble (about 0.30 per cent MgO) and 0.20 per cent Fe₂O₃. The cathode was raised and a fire-clay crucible was placed under it. This crucible was replaced after

2 hr. with another, which was also removed after 2 hr. Analyses of the material (metal in a MgCl₂-MgO matrix) are shown in Table 7.

TABLE 7.—*Analysis of Special Sludge*
PER CENT

Material	Fe	Metal- lics	B ₂ O ₃	SiO ₂
First crucible.....	1.73	13.4	0.32	0.48
Second crucible.....	1.10	21.6	0.05	0.46

After 3 hr. of catching the cathode product, the metal began to rise, and a metal recovery of 40 per cent was noted in the first hour. It should be noted (Table 7) that the B₂O₃ content of this special sludge dropped rapidly. The iron decreased somewhat and the silica not at all. This special sludge contained a large proportion of MgO and was typical of the cell sludge removed from the pilot cell when B₂O₃ was present in the cell feed.

When B₂O₃ was absent, iron was still troublesome, although less so. Contamination by iron was caused by small quantities contained in the cell feed and by attack of the cathodes and thermocouple tubes above the surface of the bath. It will be noted that in the design of the cell (Fig. 3) there are no metal surfaces above the bath level. Ordinarily when the cell was started the bath was melted directly in the cell, which led to considerable oxidation of the cathode, and it was necessary to purge the iron from the bath by adding excess feed and removing sludge from the cell. Results of a typical purge are shown in Table 8.

After 500 hr. of the test shown in Table 8, the iron in the electrolyte remained constant at 0.02 to 0.03 per cent Fe₂O₃. However, even with this low content, the magnesium contained an average of 0.3 per cent Fe. The cell feed contained an average of 0.2 per cent Fe₂O₃ and an effort was made to overcome the iron by adding MnCl₂ to the bath. The use of MnCl₂ for

this purpose was based upon the known effect of manganese on the iron content of magnesium alloys. The additions were calculated on the basis of 0.3 per cent Mn in the metal and a 100 per cent recovery. Table 9 shows that the effect on the iron was immediate. The current efficiency also increased to 70 per cent within 12 hr., despite the fact that the

and decreasing their tendency to coalesce. Globules so affected remained on the surface of the cathode until they had a complete coating of iron, magnesium oxide, and other impurities, and then fell off and sank into the sludge. It was not determined whether the iron was plated from the bath by electrolytic action or was displaced as metallic iron from some soluble form.

TABLE 8.—*Removal of Iron from Electrolyte*

Time after Start of Test, Hr.	Fe as Fe ₂ O ₃ , Per Cent	
	Sludge	Electrolyte
67	28.40	0.64
118	6.00	0.10
144	2.30	0.05
222	0.42	0.03
400	0.50	0.02

Fe₂O₃ analysis of the electrolyte remained at 0.02 to 0.05 per cent throughout the test.

Subsequently the Fe₂O₃ was reduced in the cell feed to below 0.02 per cent, to eliminate the effect of iron. Metal analyses after this change showed 0.01 to 0.06 per cent Fe.

TABLE 9.—*Effect of MnCl₂ Additions on Metal Impurities*

Duration, Days	Impurities in Metal, Per Cent		
	Fe	Si	Mn
1	0.27	0.09	0.06
2	0.35	0.09	0.14
3	0.30	0.07	0.31
4	0.07	0.05	0.15
5	0.06	0.32	0.16
6	0.04	0.25	0.23
7	0.05	0.08	0.08
8	0.07	0.15	0.22
9	0.04	0.42	0.06
10	0.02	0.39	0.15
11	0.03	0.29	0.28
12	0.03	0.17	0.23
13	0.03	0.19	0.12

The most noticeable effect of iron was that it plated from the solution as metallic iron, which was not soluble in the liquid Mg but floated on the surface of the small globules, increasing their specific gravity

Sulphate.—It has been reported¹⁷ that the presence of sulphate in the bath is particularly deleterious to the electrolysis because of its reaction with Mg to produce MgO. The odor of sulphur gas was detected in the pilot cell, but it was felt that the slight additional quantity of MgO caused by this reaction should have no bad effects. During this period cathode incrustations were noted when impurities were high, with resultant lowering of metal recovery. Analysis of these incrustations showed Fe, SiO₂, and MgO, but no sulphate. However, specific tests carried out in the relative absence of other impurities in the test cell (Fig. 3) showed that the presence of sulphate had a very marked effect on recovery of metal. This effect was manifested by globules of metal and a hard, dense incrustation on the cathode surfaces. When the sulphate content of the feed was 0.8 per cent SO₄, the removed metal sometimes consisted entirely of particles 0.10 to 0.25 in. in diameter, each particle covered with a hard shell, which prevented coalescence. More or less electrolyte was also trapped inside the shells, which normally were spherical. A fairly large proportion of the metal was lost by sinking into the sludge under these conditions. A hard, dense crust up to ½ in. thick also was formed on the cathodes and an analysis of this (Table 10) showed that it contained a much higher percentage of MgO than did the normal cell sludge.

Leached samples of the metal shells showed a higher proportion of iron and silica to MgO than was exhibited by the cathode incrustation. A typical sample

analyzed 87.8 per cent MgO, 7.4 per cent Fe_2O_3 , and 3.8 per cent SiO_2 .

TABLE 10.—*Analysis of Cathode Incrustation*
PER CENT

MgO.....	67.3
MgCl ₂	16.1
CaCl ₂	3.7
KCl.....	1.4
NaCl.....	0.1
Mg.....	7.8
Fe_2O_3	3.1
Al_2O_3	0.3
SiO_2	0.6
Mn.....	0.3
	101.5

When the sulphate content of the feed was reduced below 0.2 per cent, the effect largely disappeared and at 0.1 per cent it could no longer be detected. In the section relating to MgO, it was noted that colloidal MgO deposited on the cathode at times, and it is apparent that the sulphate in some way contributes to this phenomenon. It is possible that, instead of the sulphate reacting with Mg, a reaction takes place analogous to the one found by Johnstone and Winsche¹⁶ for the system Na_2SO_4 -NaCl-FeCl₃, in which a solid phase of $\text{Fe}_2(\text{SO}_4)_3$ was formed on addition of Na_2SO_4 to fused NaCl-FeCl₃. However, neither of these explanations accounts for the large quantities of MgO noted.

Silica.—Silica present in the cell feed was reduced to silicon at the cathode and then alloyed with the metal. When the cell feed for the pilot operations contained 0.08 per cent SiO_2 , the metal analyzed 0.07 per cent Si, and feed containing 1.5 per cent SiO_2 yielded metal with 0.20 per cent Si. The silica analysis of the normal electrolyte, however, was consistently below 0.01 per cent. Silicon in the metal was regarded as an undesirable impurity but no positive correlation was noted between this impurity and recovery of metal. However, during some experiments in the test cell (Fig. 3) Si in the metal rose to more than 1.0 per cent and metal recoveries were low. The effect could be attributed to increased specific gravity

and decreased coalescence of the globules on the cathode surface in addition to irreversible current-efficiency losses due to Mg losses in the reduction reaction.

Alumina.—No operating difficulties were noted that could be ascribed to the presence of alumina in the cell feed.

Anode Gases, Cl_2 , CO and CO_2 .—It is necessary to consider the ability of the gases Cl_2 , CO and CO_2 to recombine with Mg(l) in designing a cell. Should the cell be so constructed as to permit these gases to diffuse to the cathode, or should their solubility in the melt be appreciable and they be carried by bath circulation to the cathode in any quantity, considerable irreversible current-efficiency loss may result.

The preliminary work was based on the assumption that the anode gases could be discarded and that any capital or labor costs involved in collecting the gas from the individual cells would be eliminated. Pilot-plant work showed, however, that some chlorine would always be lost by hydrolysis and oxidation of the magnesium chloride and that it would be necessary therefore to collect the anode gases. Special efforts to prevent all evolution of chlorine did not seem to be warranted, since a small quantity of chlorine could be readily recycled to the chlorination kiln

TABLE 11.—*Typical Analyses of Anode Gas*
PER CENT BY VOLUME

Date	Cl_2	HCl	CO_2	CO	O_2	N_2^a
Dec. 15....	0.8	10.7	50.5	4.7	4.1	29.1
Dec. 16....	0.0	17.2	67.1	4.6	1.7	19.4
Jan. 15....	0.0	8.2	75.6	1.6	1.4	13.2
Jan. 16....	6.7	12.1	65.1	1.0	1.4	12.6
Feb. 15....	7.9	7.4	66.7	2.0	3.3	19.0
Feb. 16....	2.7	17.8	55.3	3.0	3.1	6.7
Mar. 15....	0.0	23.4	61.3	3.4	0.7	10.1
Mar. 16....	0.0	22.5	62.9	3.4	0.9	10.2
Apr. 22....	3.2	9.9	51.2	1.6	2.1	32.1
Apr. 23....	0.0	15.9	66.9	3.2	0.6	11.5
July 10....	0.0	16.0	69.9	0.5	1.5	9.8

^a By difference.

or the leaching plant. It was necessary to keep the anode chamber covered to prevent burning of the anodes above the

bath and to minimize losses of MgCl_2 by hydrolysis and volatilization. The anode gases were maintained under a slight pressure in the cell.

During the periods of operation, gas samples generally were taken at one-hour intervals, and analyses were made for control purposes. Table II shows typical gas analyses during several periods. Part of the CO_2 and HCl determined in these samples may have been COCl_2 , but this was never positively identified.

OTHER OBSERVATIONS

Cathode and Anode-current Density

No quantitative determinations were made of the effect of cathode current density on metal recovery. Cathode current density was difficult to determine at any specific point because of the complicated cathode construction in the various cells. It was obvious that a very high current density produced a high temperature at the cathode, resulting in volatilization and flouing of metal, while a current density below 3 amp. per sq. in. presented a large area for adverse metal-dispersing reactions, with a resultant loss in metal recovery. It has been reported¹⁸ that low current density favors the formation of finely dispersed metal.

Observations on anode reactions showed a relationship between anode current density and depolarization reactions at the anode. This effect was studied in a test cell with external heating. The relationships between current density at anode and lowest limit of concentration of MgO that just prevents the evolution of chlorine were as follows:

CURRENT DENSITY, AMP. PER SQ. IN.	CONCENTRATION OF MgO^a WT. PER CENT
2.2.....	Less than 0.4
4.4.....	0.9
6.7.....	Greater than 2.8

^a Includes soluble and insoluble MgO

Since the equilibrium solubility of MgO in the usual bath was but a few tenths of

one per cent, and since appreciable quantities of undissolved MgO caused metal dispersion and cell frothing, it was obvious that a large anode area would be most desirable. The new pilot cell (Fig. 4) was designed to utilize all of the area of the anodes below the bath surface. The partitions in the original pilot cell (Fig. 2) decreased the effective anode area so that the current density averaged about 5 amp. per sq. inch.

Bath Temperature

While it is generally considered undesirable to operate magnesium chloride electrolytic cells at temperatures in the neighborhood of $800^\circ\text{C}.$, it was necessary to operate the cells described in this paper at 800° to $815^\circ\text{C}.$ Below this range there was a marked decrease in the depolarization reactions at the anode, which is ascribed to the influence of temperature upon the rate of solution of MgO in the melt and thus upon the concentration of soluble MgO at the anode interface.

SUMMARY AND CONCLUSIONS

From the results obtained during two years of development work, the following summation can be made:

1. A magnesium cell can be operated continuously at a reasonable current efficiency using a cell feed consisting essentially of MgO . Most of the magnesium produced is derived from the MgO , but formation of sludge is a problem.

2. To permit optimum operation of the cell, the feed must contain a minimum of impurities, special attention being paid to sulphate, boric oxide, iron, and silica. The permissible limits of these impurities have been determined, and a process has been developed for preparing a feed of the desired specifications.

3. It is deduced, from available data, that the primary electrochemical reaction taking place is the electrolysis of MgCl_2 , accompanied by a secondary depolarizing

reaction at the anode-melt interface involving MgO in solution, carbon and evolved chlorine. It is likewise postulated that the reaction in the body of the melt is between MgO in solution, suspended carbon, and diffused chlorine. The magnitude of the reaction in the body of the melt is an inverse function of the MgCl_2 content of the electrolyte.

4. The MgCl_2 concentration in the electrolyte must be maintained above 55 per cent to permit desired suppression of chlorine.

5. A major cause of sludge formation in the cell is ascribed to plating out of colloidal MgO at the cathode. The exact mechanism of colloid formation is unknown but the difficulties due to it are aggravated by the presence of sulphate and perhaps water, boric oxide and iron in the feed.

6. The presence of a small quantity of B_2O_3 in the cell feed, upon prolonged electrolysis, resulted in the formation of a tough, viscous sludge layer on the cell bottom that contained enough metallic magnesium to shunt current directly between the electrodes. In addition, minor current-efficiency losses were due to the reaction between B_2O_3 and magnesium at the cathode.

7. The presence of iron in the bath results in the plating out of metallic iron on the magnesium globules formed at the cathode in such a manner as to inhibit their coalescence. This difficulty can be minimized by the addition of MnCl_2 .

8. A bath temperature of 800° to 815°C . is necessary to obtain satisfactory operation of the processes.

9. The carbon consumption in the cell is about 0.26 lb. per pound of magnesium

produced, and the principal gaseous product of the cell reactions is CO_2 . Part of the required carbon can be supplied to the cell with the feed.

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The Refractory or "Fireless Cooker" Method of Producing Magnesium

BY E. G. DE CORIOLIS*

THE development of huge production facilities and of new or improved processes for manufacturing magnesium from its raw sources has been an outstanding achievement of this war. Furthermore, at least one new method has reached a stage of pilot production that offers promise. Its potentialities seem to indicate that a reduction in cost and simplification or elimination of problems incident to the use of at least one of the present processes are quite within the realm of possibility.

Although magnesium of very high purity (99.9 per cent and higher) is obtained, and the rate of recovery reasonable (60 to 70 per cent), the ferrosilicon reduction process is open to a serious objection, which at the time its use was proposed was thought to be sufficient to raise some doubts as to its success, at least on a high production basis. The temperature range at which the reaction is carried out—namely, 2100° to 2150°F.—is very close to the failure temperature of the material of which the retort is made. It is so close that for a time it was assumed it might make commercial use of the process an impossibility.

However, at the time under discussion, the demand for magnesium was so great

that it was felt by those who had to go ahead and produce this essential metal that the emergency warranted their taking a chance on this process. Subsequent developments have fully justified the soundness of their decision.

Fortunately for the war effort, when the plants were put into operation it was discovered that although the retorts did collapse in rather short periods of time, as predicted, they could be blown back into operable shape by application of high-pressure air. This practical method of operation so relieved the situation that the problem disappeared. Nevertheless, if the process had not been successful, or the production of magnesium by the electrolytic process had not been able to keep pace with demands, our war program would have been seriously impaired.

"FIRELESS COOKER" PROCESS

For this reason a program was set up and assigned for the development of a new method that had been suggested to the War Production Board in 1941. It is believed justifiable in terming the method "new" for several reasons: (1) while utilizing the same (ferrosilicon) process as the Pidgeon, hence involving similar reactions, the type of retort or furnace is essentially different, (2) the method of operation, reaction temperatures, etc., differ materially, and, most important of all, (3) the problems to be overcome in making the process successful were not and could not have been anticipated by anything previously known about the Pidgeon process. As will be shown later, the briquetting process, the condenser, the furnace lining

This paper is based on research work done by Surface Combustion, under the supervision of the War Metallurgy Committee, for the War Production Board as "restricted" Project NRC-520. Its publication has been authorized by the Office of Production Research and Development of the War Production Board. Manuscript received at the office of the Institute Nov. 4, 1944; revised July 2, 1945. Issued as TP 1941 in METALS TECHNOLOGY, December 1945.

Listed for the New York Meeting, which was canceled.

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and other parts of the equipment, all had to be studied and revised before success was possible, even on the limited basis established by the pilot installation. It has, therefore, been deemed advisable to disclose the method at this time, especially since some of the problems overcome may be of value in other fields of development and may also indicate the path to be followed in any further development of the process.

The term "fireless cooker" was applied to the process because it most aptly indicates the general method involved in obtaining the desired result. It consists fundamentally in charging briquettes composed of dolomite and ferrosilicon (as in the Pidgeon process) into a refractory-lined, vacuum-tight steel shell, which has previously been heated to a maximum temperature of 2700°F. The steel shell is then evacuated and the heat stored in the heated refractory furnishes the necessary heat for reaction, while simultaneously cooling to a temperature of 2200°F.

The development of the process can most conveniently be divided into three parts: (1) laboratory and experimental plant development, (2) preliminary pilot-plant tests, including construction, revisions, etc., and (3) production runs, results, conclusions, future possibilities, and so forth.

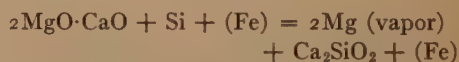
LABORATORY AND EXPERIMENTAL PLANT DEVELOPMENTS

This stage of development was on virgin ground in many ways. Very little really conclusive information was available about the metal itself, especially as to its behavior under the proposed conditions. Reaction rates and temperatures under varying conditions of vacua, heat capacities of the reacting materials and the refractories, under the high temperatures proposed, the effects of magnesium vapor on the furnace materials, means of producing high vacua rapidly, degassing of refractories, methods of sealing the apparatus, and an infinite

variety of minor design points—all were virtually unknown. The first period of the work, therefore, lasted nearly two years—until early in 1942.

PRODUCTION OF BRIQUETTES

In preparing the briquettes used in the production of magnesium the procedure is, in general, as follows. Dolomite, calcium-magnesium carbonate $\text{CaMg}(\text{CO}_3)_2$, is first calcined, leaving a residue of lump lime composed of equal molecular parts of CaO and MgO . The lime is then mixed with 75 per cent ferrosilicon in such proportions that the amount of silicon is chemically equivalent to the amount of magnesium, thus providing the following reaction:



However, it is possible to produce two distinctly different types of briquettes on this same basis; the so-called wet or dry briquettes.

The wet briquettes are made by adding water to the lime before briquetting. This produces an extremely hard and tough briquette, which is also very porous after the water is driven off by preheating. Using pure dolomite and a perfect mixture, a production of 9.5 lb. of magnesium, at 75 per cent silicon efficiency, is possible per cubic foot of briquettes. Dry briquettes are produced from dry lime, giving a comparatively fragile but compact briquette, from which a yield of 12.3 lb. of magnesium, at 75 per cent silicon efficiency, is possible per cubic foot. The advantages of wet briquettes lie in their ability to resist handling without excessive breakage, in greater reaction rates, in higher ultimate efficiencies, and in reduced briquetting pressures. On the other hand, dry briquettes give a greater yield per cubic foot of retort space, and in the Pidgeon retort process do not require preheating for drying.

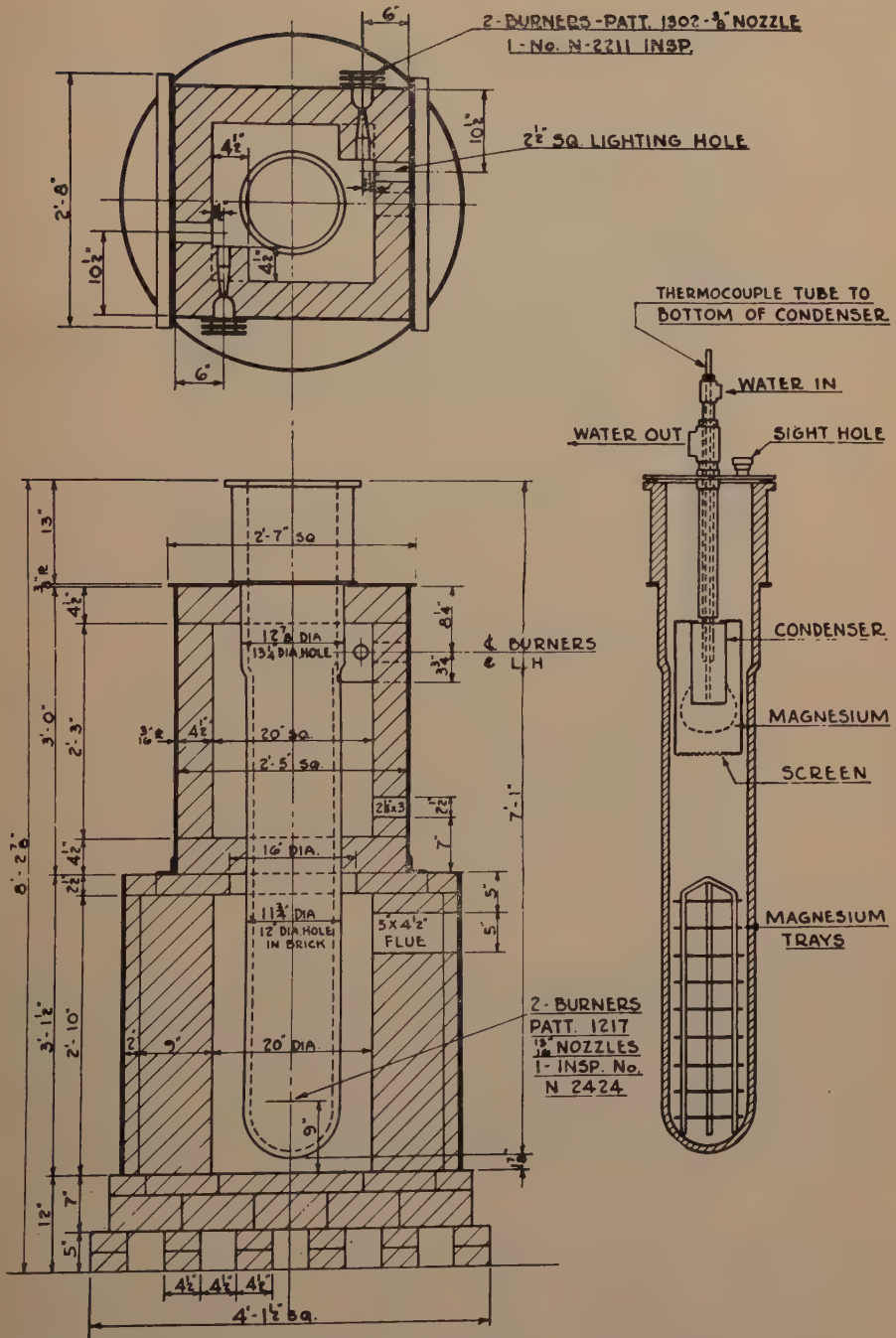


FIG. 1.—ARRANGEMENT OF CONDENSER AND TRAYS IN TUBE

REACTION RATES

Prior to the laboratory work for the fireless cooker method, nothing was known about reaction rates above 2100°F. These

tom) portion could be held at any temperature between 1500° and 2100°F., while the condensation (upper) part could be held at about 1350°F. Magnesium was distilled

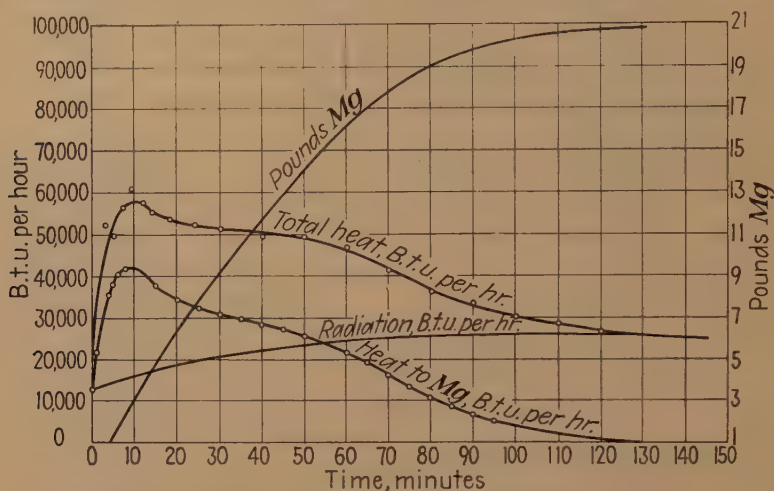


FIG. 2.—CONDENSATION TEST DATA.
Magnesium charged, 21 lb.; magnesium recovered, 20.9 lb.

tests showed the rate to increase rapidly above this temperature, becoming a virtually instantaneous reaction at 2360°F., the rate being proportional to the number of silicon-vapor molecules per unit volume. The influence of silicon and of CaO in the reaction was also found to be important in affecting the reaction rate and availability of the magnesium. The production of magnesium from pure MgO and pure ferro-silicon in which the yields were poor confirmed the effect of CaO in the dolomite.

DESIGN OF CONDENSER

Much higher production rates thus were to be expected in the refractory method than are obtained by the retort process, because of the much higher temperatures used. This immediately imposed the problem of properly designing a condenser to handle the production rate. To arrive at a condenser design, rates and temperatures of magnesium vaporization and condensation were determined in a two-zone retort or furnace (Fig. 1). The distillation (bot-

tom) portion could be held at various rates in vacuum under carefully controlled conditions.

Magnesium distillation began at a temperature of 1100°F. Condensation was instantly indicated by an abrupt rise in temperature of the condensing unit and could be followed visibly through a sight glass in the side of the retort. Normal temperature recurred when condensation had been completed. The amount of magnesium was then weighed and compared with that originally introduced. The rate of condensation, the amount of heat abstracted per pound, and the rate of heat transfer per unit area through the wall of the condenser were thus all determined before the full-scale plant was designed and built. The curves on Fig. 2 give the results of these tests.

Fig. 3 shows the experimental condenser (of 4-in. diameter) with a solid ball of magnesium condensed upon it. The sodium impurities are condensed on the upper and colder regions. At the right a ball that was



FIG. 3.—MAGNESIUM BALLS CONDENSED AT HIGH RATES.



FIG. 4.—BALLS CONDENSED BY HIGH CONDENSATION RATES.

From left to right:

- | | | |
|--|---|---|
| 1. 0.01-lb. ball produced in 1 1/4-in. dia. retort | 4. 12-lb. ball produced in 10-in. dia. retort (fractured through axial plane showing the magnesium structure) | 6. 17-lb. ball produced in 10-in. dia. retort (cut through center and polished) |
| 2. 0.5-lb. ball produced in 4-in. dia. retort | 5. Same as 4, unfractured | 7. 20-lb. ball produced in 10-in. dia. retort |
| 3. 8-lb. ball produced in 10-in. dia. retort | | |

condensed at too low a temperature is shown. It exhibits a coarse crystal-like structure. Below the large ball is one of intermediate size condensed on smaller equipment. Fig. 4 shows a variety of balls from 0.1 to 20 lb., condensed under various conditions by high condensation rates. Only pure magnesium is condensed if the temperature is above 500°F. but below the

condensation temperature of approximately 1100°F.

CHOICE OF REFRACTORY

Because of its high heat content and great conductivity, Carborundum appeared to be the ideal refractory for use in the "fireless cooker." After a number of tests it was established that this refractory could

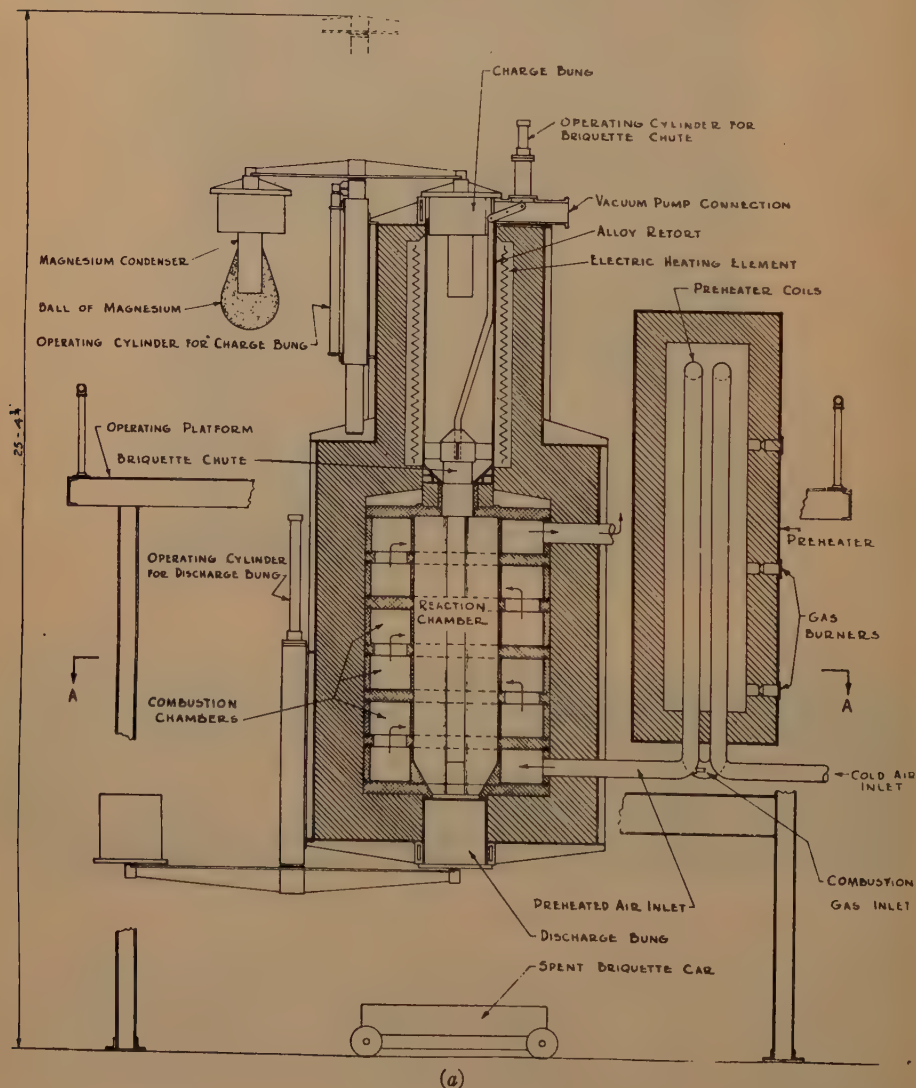


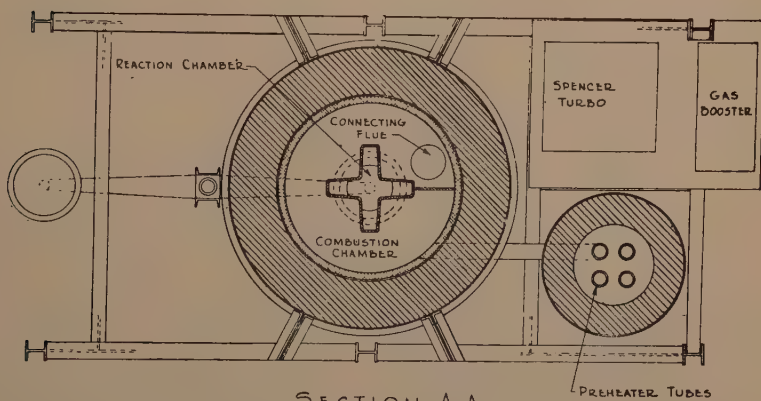
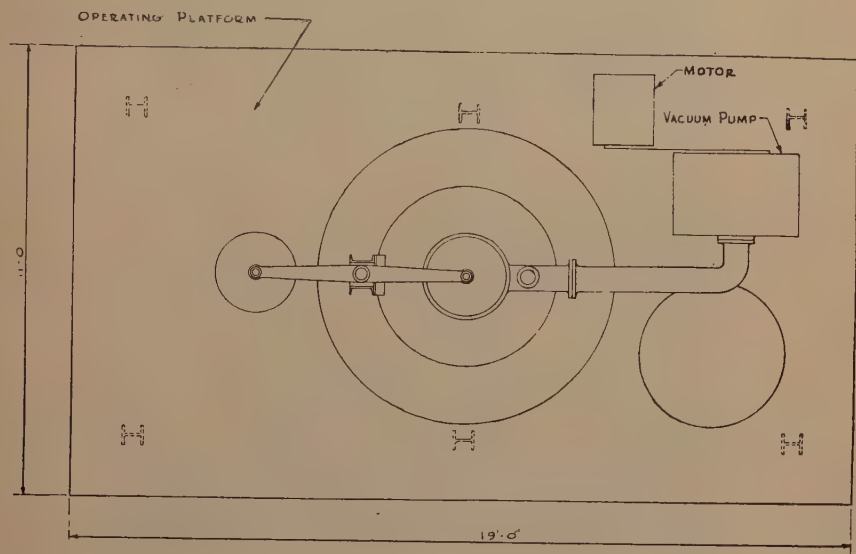
FIG. 5.—MAGNESIUM

supply heat to the charge at a sufficiently high rate, and that no deleterious reactions would occur between the refractory and the briquettes or the magnesium vapor at high temperatures. It was also established that the magnesium produced would be of a purity comparable with that of the magnesium obtained in the Pidgeon retort process.

During this period many other pertinent features of design, such as the vacuum system, the pump, and the closures, were worked out.

PILOT PLANT

Work on the pilot plant, an addition to the pilot-plant building of the Magnesium Reduction Company's plant at Luckey,



SECTION A-A
(b)

REDUCTION UNIT.

Ohio (division of National Lead Co.), was started toward the end of 1942. By January 1943 the work was completed. The unit contemplated the production of 100 lb. of magnesium per charge, with an over-all cycle of approximately 2 hr., allowing 30 min. for production and condensation of the magnesium vapor. The expected rate of production was so much higher than contemplated in the laboratory that segregation of the function of magnesium condensation from that of reaction or production was considered desirable. As later events showed, control of the former was to be a real problem. By March of 1943 the plant was completed and ready for operation.

Original Design of Equipment

Fig. 5 shows schematically the operations involved in the process. The vacuum-tight shell is fitted with four vacuum-tight hydraulically operated closures. The charge and discharge closures are at the top and bottom of the unit. Burner and flue closures are at the sides. The upper section of the unit contains an electrically heated charge-holding chamber in which the preheat temperature of the charge of briquettes is maintained prior to dumping into the high-temperature reaction chamber below. The briquettes are externally preheated to approximately 1250°F. before being placed in the upper or holding chamber. The reaction chamber is composed of a cross-shaped Carborundum muffle. Surrounding this is an annular chamber of Carborundum used for heat storage. The magnesium condenser is suspended axially from the top closure into the charge-holding chamber.

Operation

The mode of operation is as follows: The unit is first heated to a temperature of 2700°F. by burning natural gas with preheated air in the combustion space between the Carborundum muffle and the heat-storage Carborundum. The preheated air

temperature is approximately 800°F., obtained in hairpin U-shaped tubes suspended in an auxiliary furnace.

Electric heating elements maintain a temperature of from 1200° to 1500°F. in the upper chamber. During the firing period the bottom discharge closure is cleaned of all previous contamination and also made vacuum-tight. After a temperature of 2700°F. has been reached in the reaction chamber, firing is stopped, the briquettes are quickly charged, the burner and flue closures made vacuum-tight and the vacuum pump started. After the pressure in the reaction chamber has been reduced to 1 in. Hg or less, the briquettes in the charge-holding chamber are dumped by an externally, hydraulically operated valve. This part of the unit was completely revised subsequently, as described later.

During the following magnesium reduction period the magnesium vapor passes into the upper chamber and condenses on the condenser. When the temperature in the reaction chamber has fallen to 2200°F. the reaction is completed, air is allowed to re-enter the chamber, the top closure holding the condensed magnesium ball is raised above the chamber, the flue and burner closures are opened and firing is resumed. During the firing period the bottom closure is lowered and the spent briquettes allowed to fall into the spent briquette buggy. The cycle is then repeated.

Additional Features of Design and Operation

Because of frequent lack of factual data, it was necessary to project laboratory results to the full-scale unit. This entailed the imposition of safety factors, which in some cases appreciably exceeded actual requirements.

Approximately 10,000 lb. of Carborundum refractory is used to provide the heat storage capacity between the temperatures of 2700° and 2200°F. The bottom closure provides a double seal made by a tongue

and groove joint thrust home by the hydraulic cylinder. Water cooling is provided to protect all rubber gaskets, a temperature of 150° being used to prevent the condensation of water vapor from the flue gases. The shell itself was designed to oper-

temperature of 1300°F. is low, so that the life of this retort would be indefinitely long.

Condenser

The large condensers shown in Fig. 6 are the result of preliminary experiments. One

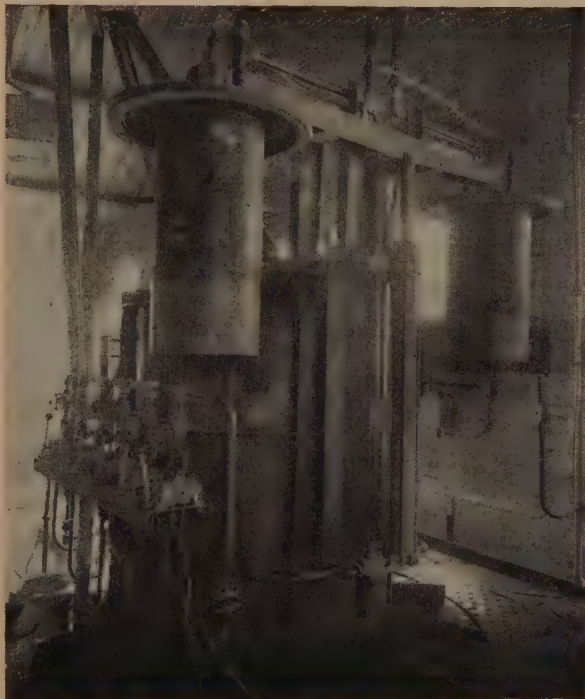


FIG. 6.—REDUCTION FURNACE. MAGNESIUM CONDENSERS IN FOREGROUND.

ate between temperatures of 200° and 300°F. (Except for the condenser and top closure shown, the drawing is accurate.)

To provide heat-exchange capacity, the Carborundum is arranged in an annular ring, so that it is possible to transfer the heat rapidly by radiation. Since there is no great thickness of the Carborundum, the material is quickly heated by the combustion gases, which are maintained at a flame temperature of 4500°F.

In the charge-holding unit at the top, a heat-resisting alloy retort of light gauge is utilized to prevent diffusion of the magnesium vapor into the part of the unit that contains insulating firebrick. The holding

is 14 in. and the other 16 in. in diameter, similar in design to the laboratory unit.

Briquette Preheating

Preheating of the briquettes prior to charging into the heat-holding chamber was accomplished in two small convection furnaces. The briquettes were placed in a cylindrical basket with a screen bottom before they were put into the furnace. Recirculated flue gases blown at high velocity through the furnace were found to be capable of heating the briquettes to a uniform temperature regardless of the diameter of the basket. The temperature was carefully controlled to prevent heating above the set temperature of the furnace.

The laboratory tests had shown that the briquettes could be heated to the proper temperature without oxidizing the ferro-silicon, and that either hydrated or com-

1943, the plant was fired, and after an initial soaking at 2300°F., to dry the brickwork, and so forth, it was heated slowly to 2800°F. Tests showed satisfactory vacua



FIG. 7.—SILICON CARBIDE CEMENT BONDING MELTED OUT OF JOINTS.

pletely anhydrous dolomite could be used. Handling of the briquettes (which were furnished from the Magnesium Reduction Company's plant near by) was facilitated by placing an automatic dump chute in the bottom of each preheating basket.

Preliminary Vacuum Tests

Vacuum tests conducted prior to initial firing showed that very satisfactory results were possible. The unit was reduced from atmospheric pressure to 0.01 in. in 8 min. The ultimate pressure of 0.0025 in. was obtained in 22 min. These tests were conducted prior to the bricking of the shell.

After completion of the tests, in March

and control operation. Radiation losses also were according to calculations.

Magnesium Produced

Early in April 1943 the first magnesium by this process was produced—some 40 to 50 lb. in from 30 to 45 min. However, the condenser temperature had been held too low and the metal was of the undesirable crystal structure. During the operation of breaking the vacuum, the metal fell into the furnace, became ignited and was lost.

As might be expected, "playing safe" resulted in overshooting the condenser temperature the second time the furnace was charged, a few days later, and some mag-

nesium condensed in the upper part of the chamber. However, its form and purity were satisfactory.

of the lower portion of the furnace at lower temperatures obviously reduced production of magnesium. It also made



FIG. 8.—SILICON CARBIDE CEMENT BONDING MELTED OUT OF JOINTS.

Slagging Problem

During these preliminary runs, a problem arose that was wholly unanticipated and was later to prove serious. In the first run, one of the cements used in the construction slagged and dripped out through the bottom bung, gluing the Carborundum face plate of the bung in its closed position. It was also discovered that when any molten slag existed in the furnace, it was practically impossible to obtain a high vacuum.

Production of magnesium during four subsequent runs brought out a number of points. The briquettes could not be completely degassed at the charge-holding temperature of 1250° to 1400°F. The rapid rate of heat transfer obtained from the storage refractory to the briquettes began the production of magnesium at pressures far in excess of 0.2 in. Hg. It was found impossible to eliminate the slagging at temperatures above 2400°F., and operation

control of condenser temperature much more difficult.

In an attempt to eliminate the slag, the entire unit was raised to a temperature of 2800°F. and held at that temperature for an entire week. Still there was no evidence that slagging had been eliminated. Tests were discontinued therefore until the cause of the slagging could be found.

Antislagging Tests and Development

Since laboratory tests had shown that pure silicon carbide (Carborundum) does not slag at temperatures even above the range of operation of the furnace, it was evident that either the cement or the refractory contained substances that did slag under the conditions of operation. Also, since some slagging had occurred before the briquettes were introduced, neither the dolomite nor the magnesium vapor could be wholly responsible.

Examination of test data from the six previous charges indicated that it was

not likely that the production of magnesium nor the vacuum was responsible for the slagging. Analyses revealed the various slags to be complex, containing silica, alumina in large proportions, iron oxide, calcium oxide and magnesium oxide. Examination of the spallac brick underneath the muffle revealed that the bulk of the slagging was coming from the combustion chamber. At no time during the operations had it been possible to detect any slag running over the inside surfaces of the muffle.

When the Carborundum muffle was removed and access to the heat-storage Carborundum was provided, it was quite apparent that the silicon carbide cement used to bond the heat-storage brick had melted out of most joints and slagged over most of the inside of the furnace (Figs. 7 and 8). Analysis of the cement used showed:

	PER CENT
Silicon dioxide.....	11.8
Silicon carbide.....	80.33
Iron oxide.....	2.80
Aluminum oxide.....	3.27
Calcium oxide.....	0.51
Magnesium oxide.....	0.55
Other impurities.....	0.80

The slag that first glued the bottom of the bung was composed of:

	PER CENT
Silicon dioxide.....	50.05
Aluminum oxide.....	23.22
Calcium oxide.....	17.60
Magnesium oxide.....	9.01
Other impurities.....	0.12

Subsequent green glassy slags were found to contain:

	PER CENT
Silica.....	61.56
Iron oxide.....	3.57
Aluminum oxide.....	24.80
Calcium oxide.....	7.48
Magnesium oxide.....	1.25

Apparently the cement did not slag as a single compound but did so in a selective manner. It appeared that the lower-melting-point substances melted out of the mixture first, followed by the others

at successively higher melting temperatures. The slagging material also seemed to become more refractory as the unit was operated. Subsequent tests indicated that the cement melted at approximately 2570°F. In all cases aluminum oxide was present in various amounts in the slags and in the peeled Carborundum. Since neither the dolomite nor the ferrosilicon contained appreciable amounts of this compound, it must have been introduced by the cement.

The investigations, which were continued for several months, showed conclusively that the "impurities," alumina and iron oxide, in the cement as a clay, were responsible for the low fusion point of the cement. It was also shown that fusion would have occurred even if the furnace had never been exposed to vacuum at the high temperatures of operation or to the attack of magnesium vapor. Cements free from these materials, also a number of zirconium silicate cements and refractories, were next tested.

Unfortunately, the zircon cements, although quite satisfactory otherwise, showed evidence of attack by magnesium vapor. Hence their use was not possible. However, purified silicon carbide cements were developed, which contained none of the clay ordinarily used as a binder—i.e., less than 3 per cent impurities—whereas the former cement had contained up to about 7 per cent. The interior of the unit was also rebuilt with entirely new Carborundum brick. Eventually a purified cement containing less than 2.5 per cent total aluminum and iron oxides was obtained and proved stable at temperatures as high as 2850°F.

Tests on the effect of the briquettes on the silicon carbide cements, glasses and brick brought out a new point. Although dolomite powder showed a tendency to fuse, it did not attack the unglazed brick, but it did attack the glazed brick. Also, it was noted that while the briquettes

did not attack the unglazed brick at first, they did so when fusion of the ferrosilicon occurred. Attack on the purified cement was noted as well. Previous experience had demonstrated that the briquettes could not be fused in vacuum at 2700°F., but that if the ferrosilicon were oxidized the briquettes would fuse at that temperature. It was, therefore, to be expected that if the ferrosilicon in the briquettes is kept from oxidizing in the unit, by discharging directly after the vacuum is broken, no rapid attack will occur.

Revisions to Condenser

Concurrent with the solution of the cement-slugging problem, work was conducted toward revising the condensing system. The new condenser was 8 in. in diameter instead of 14 and 16 as previously. Precautions also were taken to make sure that the vapor would be directed against the condensing surface. The top of the charge-holding chamber was necked down so that there was but 3-in. clearance between the condenser and wall of the chamber. The electric heating elements were relocated, to afford better heat control. The bottom bung was reconstructed, to avoid possible sticking.

Measurement of Magnesium Condensation Rate

The previous method of observing the rate of magnesium condensation by means of a sight glass was far from adequate. In order to follow the condensation process more accurately, a heat exchanger was provided to measure the heat increment in the cooling water that was recirculated through the condenser, the heat in turn coming from the condensation of the magnesium vapor on the condenser surface. The system provided a reasonably accurate method of following reaction

progress and afforded a tool for comparing the production rate of the unit under a variety of operating conditions.

Revised Charging Method

It had been found that the time required to evacuate the unit with the briquetter in the upper chamber was unduly long, requiring about 30 min. Furthermore, after reaching a comparatively low pressure before the charge was dumped, the rate of evolution of the gases from the charge into the reaction zone was so great that the pressure quickly rose to one inch after the charge was dumped. This indicated that the degassing accomplished in the upper chamber was not sufficient and actually of little value in shortening the time to attain high vacuum.

Accordingly, the method of holding the charge in the upper "holding chamber," as originally developed, was eliminated and the charge dumped directly into the reaction zone at atmospheric pressure. The revised method made it possible to dump the charge quickly and to place the unit under vacuum within less than one minute after dumping.

"Production" Runs

Revisions were completed and the unit was refired in October 1943. By the middle of the following month some seven charges had been made in the unit. In each the structure of the magnesium was good. Yields up to 60 per cent on the ferrosilicon basis were obtained. The magnesium production rate was carefully determined as a function of time. The condenser proved to be of correct size and under certain conditions operated satisfactorily.

Up to this time and during these runs wet briquettes were used. The charges were dropped into the reaction chamber under atmospheric pressure, yet in all cases evacuation rates were more rapid than those previously obtained. The

ultimate vacuum obtained was considerably improved. No difficulty was experienced with slagging of either the cement or Carborundum brick.

until the vacuum is broken. The production efficiency of 41.5 per cent on the silicon basis was obtained after about 150 min. under vacuum. Although times up to 4 hr.

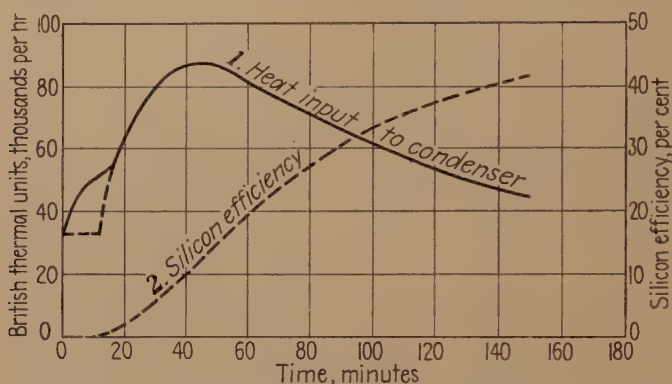


FIG. 9.—RATE OF MAGNESIUM CONDENSATION AND SILICON EFFICIENCY AS A FUNCTION OF TIME WITH CHARGE OF WET BRIQUETTES.

Wet versus Dry Briquettes

Tests with Wet Briquettes.—The normal charges as previously used were composed of 650 lb. of wet briquettes mixed in the molecular ratio of 1.1 MgO in the calcined dolomite to 1 Si in the 75 per cent ferro-silicon. Approximately 150 lb. of water vapor and other volatile matter was contained in each charge. The available magnesium per charge was approximately 92 lb. After preheating in the convection furnace at 1250°F., the briquettes were dumped directly into the reaction zone according to the revised method, the temperature of the furnace being 2650°F. In all, 16 charges were made. All were the same except that conditions of the condenser and upper chamber were varied in attempting to control the form of magnesium condensation and sodium separation. Fig. 9 shows a chart of the rate of magnesium condensation and silicon efficiency as a function of time, using wet briquettes. Briefly, the curve indicates that magnesium condensation starts about 10 min. after charging, reaches a maximum after 40 min. and then decreases slowly

under vacuum gave efficiencies as high as 60 per cent, a study of the heat input to the charge showed that much more than 40 per cent efficiency should have been obtained in the shorter period. The reason for the lower efficiency, therefore, was difficult to understand.

During these runs it was only when poor magnesium efficiencies were obtained, leaving unreacted ferrosilicon in the charge, that difficulty in removing the spent briquettes was experienced. Under such conditions the silicon would burn when the vacuum was broken, generating excessively high temperatures, which tended to fuse the briquettes together. Efficiencies higher than 50 per cent gave no trouble.

Diffusion of magnesium through the bottom alloy seal when the metal condensed on the bottom closure was also a minor problem. It was eliminated by proper adjustment of the spring holding the seal plates together. Natural gas was introduced in one attempt to eliminate this trouble, but was of doubtful success, although it did result in a slightly higher magnesium production per charge.

Tests with Dry Briquettes.—The dry briquettes were preheated to 1000°F . for $\frac{1}{2}$ hr. and the charge was dumped directly into the reaction zone, as before.

the reason for the low rates of production and low efficiencies could be determined, the entire unit and project were doomed to failure. However, since the rate of heat

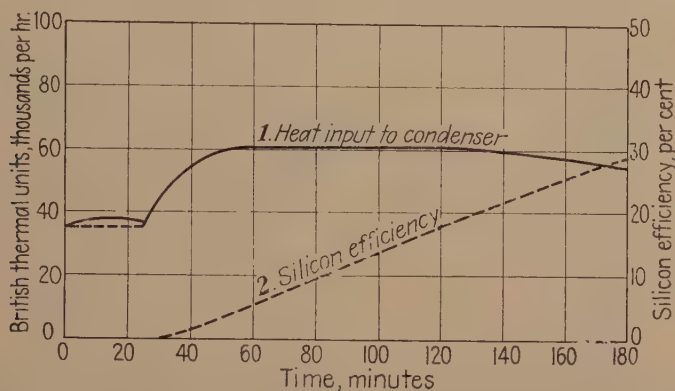


FIG. 10.—RATE OF MAGNESIUM CONDENSATION AND SILICON EFFICIENCY AS A FUNCTION OF TIME WITH CHARGE OF DRY BRIQUETTES.

The charges were composed of 500 lb. of dry briquettes in the molecular ratio of 1 MgO in calcined dolomite to 1 Si, giving about 100 lb. of magnesium per charge.

The results were far inferior to those with the wet briquettes, both as to the production rate and efficiency. Magnesium condensation began 25 min. after charging, attained a maximum after approximately 50 min. and continued practically constant for 130 min. At the end of 150 min. the total production was only 24 per cent on a silicon basis, compared with 41.5 per cent for the wet briquettes. Only 29 per cent was obtained after 180 min. These results are shown in Fig. 10. Because of the low efficiency, it was difficult to discharge the spent briquettes from the furnace. The low efficiencies obtained with these briquettes are attributable to the fact that they tend to break easily, causing poor charge porosity.

Venting the Charge

The poor results with wet and dry briquettes clearly indicated that unless

transfer had proved satisfactory, the only theory that could account for the low returns lay in the difficulty of obtaining magnesium diffusion, as suggested by the differences between the efficiencies with the wet and the dry briquettes. Therefore, a means of coring a space through the briquettes was developed.

For the first venting test a water-soaked wooden core, built into the shape of a tube, was used. The wood was first placed in the reaction zone, the briquettes poured around it, and the furnace evacuated. Although the wood burned furiously, it held shape long enough to provide the desired core throughout the test. During the test the magnesium production rate rose so rapidly that the set capacity of the condenser heat exchanger was exceeded and it was necessary to vent the steam to the atmosphere. Although it was, therefore, impossible to follow the reaction rate throughout the test, the result demonstrated that venting of the charge was extremely important. Therefore, a more practical method of venting was developed.

A steel pipe, drilled with seventy $\frac{1}{2}$ -



FIG. 11.—DRILLED 3-INCH-DIAMETER PIPE USED AS CORE FOR MAGNESIUM VENTING.

in. holes and made in three sections (Fig. 11) was used in the next test. By lowering this core into the furnace, then immediately dumping the charge around it, the tube was not exposed to oxidation until the vacuum was broken. In the tests on coring the charge consisted of 525 lb. of wet briquettes similar to those used previously, the charge now containing approximately 74 lb. of magnesium.

The results proved the soundness of the theory. Magnesium production was well started at the end of 10 min. The maximum rate of condensation of 111,000 B.t.u. per hour was attained at the end of 30 min., as compared with the previous maximum without the core of 87,000 B.t.u. per hour at the end of 40 min. Furthermore, the silicon efficiency was increased from the previous value of 41.5 per cent without the core to 55 per cent with the core at the end of 150 min. (Fig. 12).

Since the question arose as to whether or not some increase in over-all efficiency might not have occurred because there was no necessity for transferring heat to the briquettes formerly occupying the space now taken up by the core, a subsequent test was made to check this possibility. The core pipe was replaced by one having twice as many holes but exactly similar otherwise. The results showed that magnesium production began at the same time as with the former pipe core, but the maximum production rate obtained was 139,000 B.t.u. per hour. Total production was also tremendously increased. At the end of 150 min., the efficiency was 70 per cent, an increase of 63 per cent over operations when no core was used and 27 per cent above that with the former steel core. Not only was it obvious that the briquettes formerly contained in the core could have no effect, but the cause of previous low efficiencies was eliminated.

Subsequently, larger cores were tried.

Dry briquettes were also used, with an increase in efficiency, but still not equal to that obtained with the wet briquettes. Figs. 13 and 14, corrected for differences

Repeatedly different amounts of heat per unit time had to be abstracted from the magnesium vapor by the condenser, and under such conditions control was difficult.

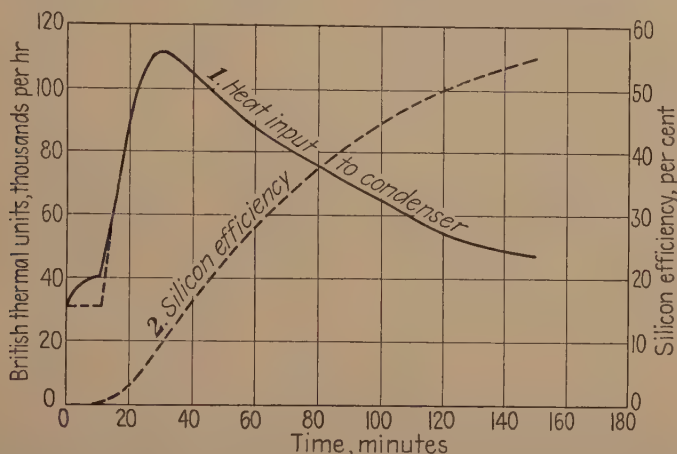


FIG. 12.—RATE OF MAGNESIUM CONDENSATION AND SILICON EFFICIENCY AS A FUNCTION OF TIME. Charge of wet briquettes using 3-inch-diameter pipe core with seventy $\frac{1}{2}$ -inch holes.

in charge size, summarize all results obtained in the coring tests. No further rise in efficiency was noted when using larger coring.

Condenser Tests

Although primary attention throughout the tests was paid to increasing efficiency and total capacity of the furnace, the condenser problem, while secondary, remained extremely troublesome. Nor was it completely solved at the conclusion of the tests.

While the quality of magnesium produced and the location of most of it on the condenser were quite satisfactory in numerous tests, there was frequently a deposition of the metal admixed with sodium on the colder part of the condenser. At times this was caused by the deposition of calcium salts on the inside of the condenser from the boiling of hard water.

Two major factors contributed to the condenser difficulties. In the period of development just ended remarkable changes in production rates were induced.

The other difficulty arose from the fact that production began so soon after the dumping of the charge. Because of this, magnesium condensation began at a pressure of 0.4 in. Hg and a considerable amount was condensed before the pressure had dropped to 0.08 in., 15 min. after the start of production. Under such conditions the velocity of gases past the condenser was so great that the magnesium vapor was carried past the part of the condenser on which it would have condensed under diffusion-flow conditions. This gave rise to the admixture of sodium with magnesium on the upper part of the condenser, thus causing both a loss in production and a fire hazard.

Various baffles were used to force the magnesium to condense on the proper part of the condenser, but although this worked very well at first another condition soon developed that prevented the successful application of the principle. Magnesia and other foreign matter had gradually accumulated in the channels connecting the heat-storage chamber with the evacua-

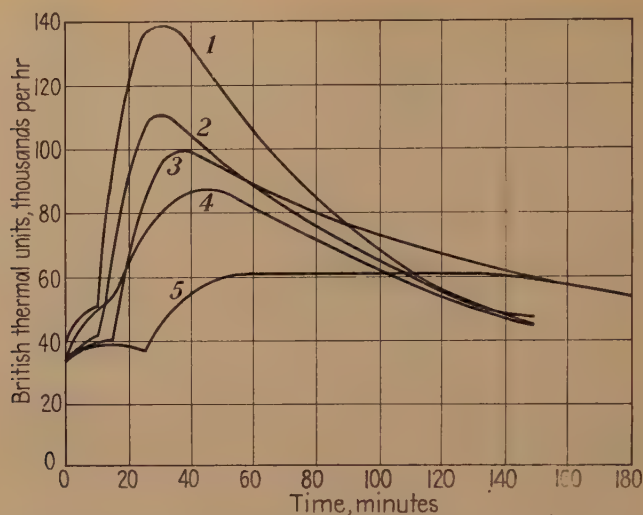


FIG. 13.—RATE OF MAGNESIUM PRODUCTION AS A FUNCTION OF TIME.
 1. Charge, wet briquettes using 3-in. dia. pipe core with 140 $\frac{1}{2}$ -in. holes.
 2. Charge, wet briquettes using 3-in. dia. pipe core with 70 $\frac{1}{2}$ -in. holes.
 3. Charge, dry briquettes using 3-in. dia. pipe core with 140 $\frac{1}{2}$ -in. holes.
 4. Charge, wet briquettes using no core.
 5. Charge, dry briquettes using no core.

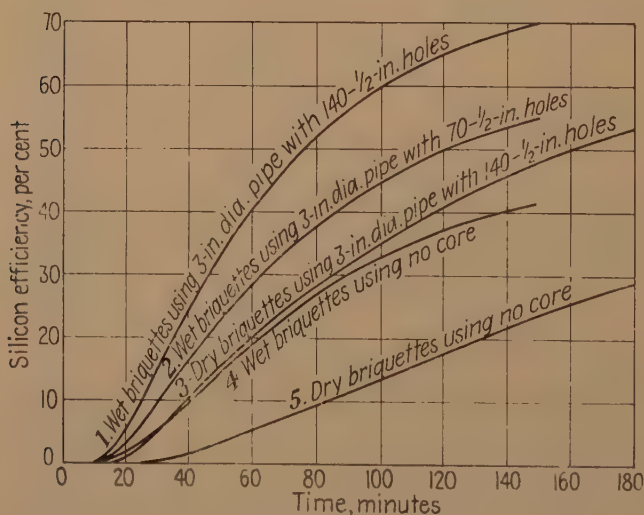


FIG. 14.—SILICON EFFICIENCY AS A FUNCTION OF TIME.

tion system, finally entirely closing them. From this time on all evacuation had to be accomplished through the condenser chamber. This slowed the rate of evacuation, but, more important, it caused a high-pressure condition at the condenser when baffles were used. This condition gave rise to a very undesirable, crystalline structure of the magnesium.

During this period the condensed magnesium was of such a form that part of it very often fell from the condenser into the reaction zone. When this occurred the magnesium revaporized at extremely high rates, thus making control of the condenser almost impossible. Furthermore, the vaporization was so rapid that local pressures as high as one half an atmosphere were generated. This is a sufficiently high pressure to produce molten magnesium and to cause it to come into contact with the Carborundum refractory. At times it was necessary to break vacuum while the magnesium was still in the reaction retort. At these times local temperatures as high as 3000°F. were generated in the retort by the combustion of the magnesium. It was these occurrences that eventually weakened a small section of the reaction retort just at the top of the charges. Finally, when the thirty-sixth charge was made, the briquettes broke through the weak section and made further operation impossible.

DISCUSSION OF RESULTS

Although compelled to discontinue the tests, a total of 34 completed runs assures that a number of facts were definitely established. Correlation of results of heat-test records showed that the heat available for the reaction was ample, about 77 per cent of the total used going into magnesium production.

In the design of the furnace it had been thought that the problem of heat transfer from the refractory to the briquettes would be a difficult one. Operation of the

furnace proved, however, that a factor of major importance might materially alter this assumption. When under vacuum and producing magnesium, the magnesium vapor particles apparently transfer heat at an enormous rate compared with ordinary radiation and conduction. It seems probable that the problem of heat transfer to the briquettes is not such a major problem as was first thought. If vertical or large-diameter horizontal retorts are employed, the problem may be only secondary to that of properly venting the charge. Venting is highly important. This incidentally leads to the question of whether or not the long, small-diameter retort used in the Pidgeon method is really concerned with heat transfer, or with the venting of the magnesium produced. When using a horizontal charge as in this process, there is always a space above the briquettes, which can serve as a channel for the vapor to escape. Hence, the distance the vapor must diffuse is less than the diameter of the retort.

Very few difficulties were experienced with vacuum. Only if excessive dust accumulates during pouring, as with the dry briquettes, can the accumulated dust slow down the rate of evacuation. In general, all vacuum seals, closures, and other parts were satisfactory.

The work has demonstrated that pure, solid structures of good magnesium can be deposited at pressures as high as 0.06 in. Hg if the temperatures are held approximately right. Sufficient data have been accumulated to make it possible to design a new condenser that would provide the necessary characteristics.

Certain conditions cause some slagging and corrosion on the inside of the retort. If the briquettes are allowed to remain in contact with silicon carbide at temperatures in excess of 2600°F. while in contact with air, there is a tendency to melt the briquettes and make them flow over the refractory. The iron and silicon

in the briquettes oxidize and form a compound that fuses in air at about 2600°F. Little difficulty of this kind was noticed with the wet briquettes, however. This caused no trouble with the type of bottom seal later used. The only severe corrosion occurred when magnesium dropped from the condenser and melted, as noted previously. The spent briquettes run freely out of the discharge bung when the production efficiency is 60 per cent or higher.

The work carried out to date indicates that the time required to heat the furnace from the lower temperature to the higher, 2200° to 2700°F., is approximately $\frac{3}{4}$ hr. Taking the reaction time for wet briquettes as $2\frac{1}{2}$ hr., the total cycle would be $3\frac{1}{4}$ hr. With slightly more effective venting, it is reasonable to expect an increase in efficiency of 5 per cent, from 70 to 75 per cent, so that with a total production of 100 lb. of magnesium per charge, the hourly production would be 31 lb. While this is somewhat less than originally contemplated, it is nevertheless quite satisfactory. This time is figured on the elimination of the preliminary degassing operation within the holding chamber, although degassing within the reaction chamber does have an effect upon the deposition of sodium on the condenser along with the magnesium.

Although planned as a part of the original program, no tests were run using excessive amounts of ferrosilicon or with fluorspar as a catalyst. Since a strong possibility existed that either of these methods of increasing production might cause excessive slagging and ruin the muffle, their use was postponed in favor of other lines of inquiry. Their use offers a possibility for future investigation.

POTENTIALITIES OF THE REFRACTORY-CHAMBER PROCESS

Although it is not possible to design the details of a large commercial furnace,

or to estimate accurately its production capacity and cost of operation without further information concerning the factors in question, it is possible to give the fundamental features of design that must be incorporated into such a furnace and make a rough estimate of the economics of the process.

Assuming that the difficulties that still remain unsolved can be corrected in the future, it should be practical to construct a furnace capable of producing between 500 and 1000 lb. of magnesium per charge.

It is conservative to expect that, when using wet briquettes of equimolecular mix, a silicon efficiency of 75 per cent can easily be attained. This would require 8300 lb. of wet charge containing 23 per cent water to produce 1000 lb. of magnesium. From previous operations, it is conservative to estimate that an efficiency of 75 per cent could be obtained in 4 hr. under vacuum, and that the furnace could be reheated to reaction temperatures in 2 hr., utilizing at least 1000°F. preheated air. The production capacity of the furnace, therefore, would be 1000 lb. of magnesium in 6 hr., or 4000 lb. per 24-hr. day. This furnace, producing 1000 lb. per charge, would therefore be roughly equivalent in capacity to 40 alloy retorts of the type now used in the Pidgeon process.

Obviously, it is not possible to place too much confidence in estimated costs. However, it is felt that the estimates that have been made are conservative, and that they indicate that the refractory-chamber method shows the potentiality of surviving competition with other processes for production of magnesium.

ACKNOWLEDGMENTS

The process was developed by Dr. J. J. Turin, now Ensign, U.S.N.R., with the collaboration of Jack Huebler. Design of the unit installed at Luckey, Ohio, was by A. W. Peters.

Magnesium from Olivine

By E. C. HOUSTON,* MEMBER A.I.M.E.

THE presence in the Tennessee Valley of extensive deposits of olivine, a silicate of magnesium and iron that contains approximately 28 per cent magnesium, has been recognized since 1896 when Lewis⁶ published a survey of basic magnesium rocks of western North Carolina. A recent field survey by T.V.A.⁷ showed that more than two hundred million tons of high-grade olivine occurs above local drainage levels in western North Carolina and northern Georgia.

Except for sporadic attempts to work the olivine for its nickel and chromium contents,¹⁰ the ore received little attention industrially until 1926 when Goldschmidt³ suggested its use in the manufacture of refractories. Only one instance is recorded of an attempt to utilize the ore commercially for its magnesium content;¹¹ in this case a process was used in which olivine was treated with sulphuric acid, the resultant mixture was leached with water, and the leach solution was purified and evaporated to form epsom salts, which was the end product.

As a part of its program of contributing to the development of the natural resources of the region, the Tennessee Valley Authority became interested in the olivine deposits as a source of metallic magnesium because of their high magnesium content and proximity to hydroelectric power. Studies were undertaken to determine the feasibility of producing magnesium chloride by

extraction of olivine. The experimental work was carried out successively at the T.V.A. Minerals Testing Laboratory, Norris, Tenn., at the Georgia State Engineering Station,* Atlanta, Ga., and at the T.V.A. laboratory at Wilson Dam, Ala. The present paper describes a process, developed through the pilot-plant stage, whereby magnesium chloride suitable for reduction to metallic magnesium can be prepared from olivine by extraction with hydrochloric acid and subsequent purification.

Research on the magnesium-from-olivine process, originally intended for peacetime use, was given impetus by the shortage of magnesium that existed at the beginning of the current world war. By the time the process was sufficiently developed to justify a proposal for its inclusion in the war program, the shortage had been met by expansion and development of other processes. However, it is believed that the magnesium-from-olivine process may have advantages that will warrant consideration of its use after the war, when the economics of the various processes rather than production on a wartime scale will be the criterion for commercial production of magnesium.

DESCRIPTION OF PROCESS

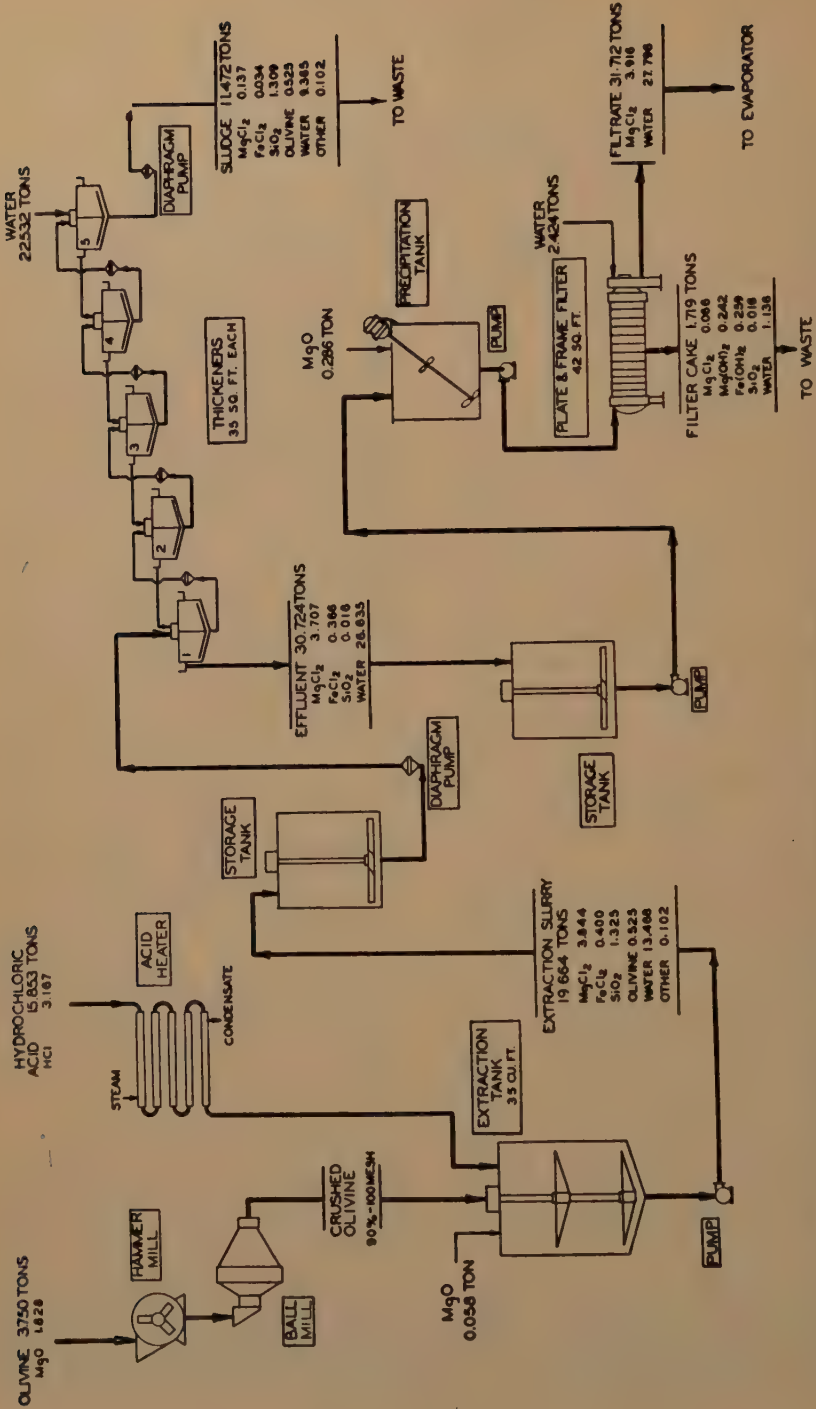
Metallic magnesium is produced electrolytically by the Dow and the Elektron

Manuscript received at the office of the Institute Nov. 2, 1944. Issued as TP 1828 in METALS TECHNOLOGY, April 1945.

* Chemical Engineer, Tennessee Valley Authority, Wilson Dam, Alabama.

⁶ References are at the end of the paper.

* Equipment, facilities, and consultant services of the staff of the Georgia State Engineering Experiment Station were made available through a cooperative agreement between the Georgia State Engineering Experiment Station and the Tennessee Valley Authority.



NOTE: ALL VALUES GIVEN ARE BASED ON THE PRODUCTION OF ONE TON OF Mg PER 24 HOURS

FIG. 1.—FLOWSHEET FOR PRODUCTION OF MAGNESIUM CHLORIDE BY EXTRACTION OF OLIVINE WITH HYDROCHLORIC ACID.

processes. The process developed by T.V.A. produces a partially hydrated magnesium chloride suitable for reduction by the Dow process. Since the Elektron process requires an anhydrous cell feed, the magnesium chloride produced by the T.V.A. process cannot be used in the Elektron-type cell. At present, magnesium chloride for reduction by the Dow process is prepared by methods¹³ that include evaporation and fractional crystallization of brines; chloridization of dolomite and of sea-water magnesia by treatment with hydrochloric acid; and treatment of dolomite with a soluble chloride, usually by-product calcium chloride. When hydrochloric acid is used to prepare magnesium chloride, the acid is made from the chlorine obtained from the reduction of magnesium chloride. The various processes have been described in the literature, and it is not within the scope of this paper to review them at length. It is apparent, however, that the present methods for preparing magnesium chloride cell feed of suitable purity and without excessive loss of hydrochloric acid are not simple.

The process developed by T.V.A. for the production of magnesium from olivine consists of the following principal steps.

1. Finely ground olivine is extracted with aqueous hydrochloric acid to produce an impure magnesium chloride solution and a residue consisting principally of silica.

2. The siliceous residue is separated from the solution by continuous countercurrent decantation in thickeners.

3. Magnesia is added to the clarified impure solution to precipitate the iron and minor impurities as hydroxides, and the precipitate is separated from the solution by filtration.

4. Magnesium chloride cell feed is prepared from the purified solution by evaporation and dehydration.

5. The dried magnesium chloride is charged to an electrolytic cell to produce metallic magnesium and chlorine gas.

6. The chlorine gas is converted to hydrochloric acid by reaction with steam and coke, and the acid is recycled to step 1.

Although the pilot plant used in the study of this process included equipment for carrying out all these steps, the experimental work was directed principally toward development of the first three steps, in which the process necessarily differs from other chloride electrolytic magnesium processes. Fig. 1 is a quantitative flow-sheet, based on a 6-week period of operation of the part of the pilot plant that is operated for the production of purified magnesium chloride solution from olivine. The pilot plant had a capacity of 700 lb. of magnesium chloride (13 per cent solution) per 24 hr. Fig. 2 is a general view of the pilot plant showing the extraction, purification, and reduction units. Since preparation of magnesium from the purified solution and conversion of the resulting chlorine to hydrochloric acid (steps 4, 5, and 6) were carried out by methods commonly used in other processes for producing magnesium, only a brief description of the methods used in carrying out these steps in the pilot plant is presented in this paper.

THE OLIVINE USED

Olivine, a mineral of igneous origin, consists of a solid solution of magnesium and ferrous orthosilicates and usually is designated by the formula $(\text{MgFe})_2\text{SiO}_4$. It is light green, has a specific gravity of 3.2, and resembles some types of sandstone in that it has a granular, friable structure.

The olivine used in this work was obtained as a carload lot in the form of 4-in. to 6-in. lumps. It had been quarried from a deposit near Balsam, N. C., which had been shown by a field survey⁷ to be typical of high-grade olivine available at several localities in western North Carolina. The Balsam deposit was estimated to contain 17 million tons of essentially unaltered olivine. The composition of this olivine, as determined chemically and spectrographically, was:

CONSTITUENT	PER CENT
MgO.....	48.71
SiO ₂	41.08
FeO.....	7.06
Fe ₂ O ₃	1.28
Cr ₂ O ₃	0.50
CaO.....	0.00
Al ₂ O ₃	0.04
NiO.....	0.44
MnO.....	0.18
Cu.....	< 0.01
B.....	Not detected
Ignition loss.....	0.47
Total.....	99.77

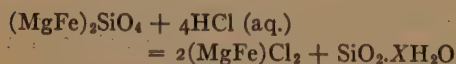
Petrographic analysis⁷ showed that the olivine was of crystal size ranging from about 0.1 to 5 mm. It contained a small amount of chromite and magnetite, occasional small crystals of chlorite, and thin seams of chrysotile.

The olivine was crushed in a jaw crusher to about 1-in. size and was then run through a hammer mill that reduced the ore to sand sizes in one pass. The product of the hammer mill was similar to quartz sand in grindability. It was ground in a ball mill and was dry-screened through a 100-mesh sieve. In preparing this olivine and in working with other samples of olivine, it was noted that the chromite was considerably harder than the olivine. This difference in hardness, which resulted in differential grinding and a concentration of chromite in the oversize, suggests the possibility of obtaining a saleable chromite concentrate as a by-product.

EXTRACTION

Laboratory Results

The reaction between olivine and hydrochloric acid may be represented by the equation:



Maximum conversion of hydrochloric acid to magnesium chloride was considered

more important than maximum extraction of magnesium from olivine, because any acid not converted to magnesium chloride during extraction would have to be neutralized with magnesia, which is relatively expensive. Consequently, the principal objectives for the extraction were: (1) to convert as much as possible of the hydrochloric acid to magnesium chloride, (2) to produce the siliceous residue in a nongelatinous form, in which it could be readily separated from the solution, and (3) to extract as high a percentage of magnesia from the olivine as was consistent with the first two objectives.

Preliminary work⁸ showed that the second objective—that is, the separation of silica—could be attained by a method that consisted of absorbing hydrogen chloride gas on the moistened surface of olivine particles. The magnesium chloride so formed was recovered by leaching, which left a residue of silica and unextracted olivine. Further studies of this method showed that inherent mechanical difficulties prevented efficient utilization of acid and olivine. The method was abandoned because of these difficulties, and the present process for extracting fine-ground olivine with aqueous hydrochloric acid was developed.

Preliminary extraction tests made with varying proportions of olivine and hydrochloric acid showed that it was feasible to extract about 86 per cent of the magnesium from olivine and simultaneously to obtain about 97 per cent reaction of the acid to form chlorides of magnesium and iron. The preliminary tests showed that, regardless of the ratio of acid to olivine used in the extraction, the mol ratio of magnesium to iron in the extract was about 12, which was approximately equal to the mol ratio of magnesia to ferrous oxide in the olivine; this indicated that the extraction was not selective.

The settling rate and bulk density of the siliceous residue were increased by increasing the concentration of the acid used and

the temperature of extraction; both factors had a dehydrating effect on the silica formed. An acid concentration of 20 per cent HCl was found to be sufficiently high

with vacuum applied for 30 min. The degree of hydration of the silica residue in these tests, as determined by drying at 120°C ., decreased from about 35 to about



FIG. 2.—PILOT PLANT FOR EXTRACTION OF MAGNESIUM FROM OLIVINE.

to permit production of the silica in a favorable condition for separation by settling. Higher concentrations, though beneficial to the settling properties of silica, caused difficulty due to loss of acid as fume. It is feasible to produce acid of 20 per cent concentration from magnesium chloride reduction-cell gases,⁹ but it was questionable whether these gases were suitable for the economic production of acid of higher concentration.

In a series of tests in which the acid concentration was 20 per cent HCl and the extraction temperature was varied, it was observed that the residue produced had good settling properties when the temperature was in the range 90° to 110°C . Samples of the residue were separated from the solution by filtering on a Buchner funnel; the residue was washed with water and then was allowed to remain on the filter

20 mols of H_2O per mol of SiO_2 when the temperature of extraction was increased from 60° to 105°C . The residues produced at the lower temperatures were of large bulk, because of their high degree of hydration, and did not settle well.

Tests of the effect of temperature on percentage of magnesium extracted from olivine showed that when the temperature was increased from 70° to 110°C . the amount of magnesium extracted increased from 30 per cent to 80 per cent at an extraction time of 30 min. (Fig. 3). Although it was possible to extract a satisfactorily high percentage of magnesium from olivine at temperatures in the range 80° to 100°C . with prolonged extraction, extended extraction periods at temperatures much below 100°C . were undesirable because these conditions tended to produce a gelatinous type of silica. When extraction was

carried out at or near boiling temperature, the reaction was practically complete in 30 min. or less, and the residue had good settling properties.

that could be pumped readily; unagitated mixtures yielded a stiff, gelatinous mass. It was desirable to add the acid and olivine to the reaction vessel simultaneously while

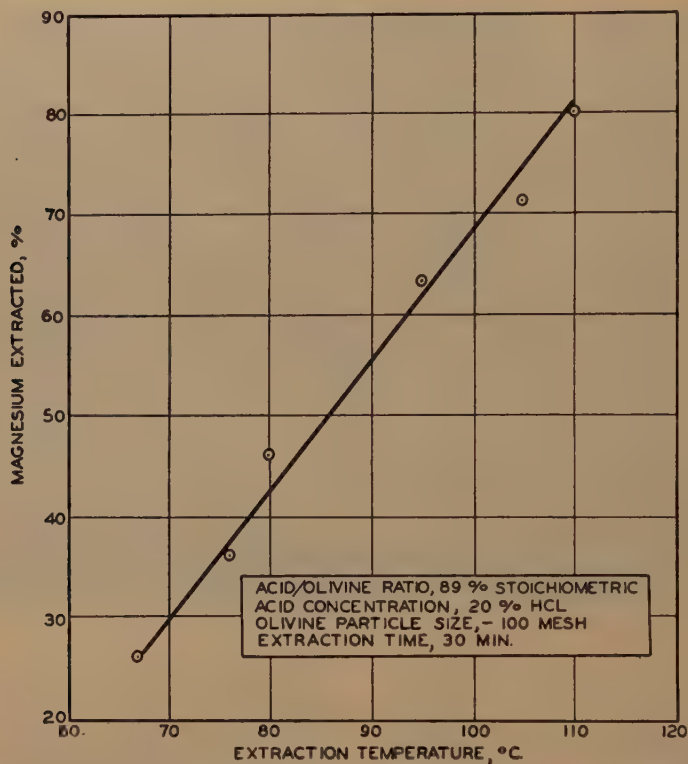


FIG. 3.—EFFECT OF EXTRACTION TEMPERATURE ON PERCENTAGE OF MAGNESIUM EXTRACTED FROM OLIVINE WITH HYDROCHLORIC ACID.

Since the reaction between olivine and hydrochloric acid is exothermic, it was convenient to utilize the heat of reaction to raise the temperature of the mixture to boiling. To start the reaction at a sufficient rate to induce boiling, it was usually necessary to preheat either the olivine or acid. Preheating the acid to about 60°C. was generally sufficient to cause boiling of the reaction mixture in uninsulated vessels. It was not practical to use heating coils in the reaction vessel because a silica scale deposited on the heated surfaces.

Thorough agitation during the reaction was essential for production of a fluid slurry

maintaining good agitation; this procedure released the heat of reaction gradually and prevented too vigorous boiling or foaming. The particle size of the olivine was relatively unimportant in all sizes finer than 100 mesh. Larger sizes were difficult to keep in suspension during extraction.

Pilot-plant Operation

Data from the small-scale tests were used in designing a pilot-plant extraction unit. Particular attention was given to use of materials of construction that would be adaptable to commercial-scale operation. The extraction vessel was a cylindrical steel

tank lined with Pyroflex and acidproof brick; the tank was 65 in. high and had an inside diameter of 45 in. Four bricks projected $4\frac{1}{2}$ in. from the walls into the tank to serve as baffles. A 1-in. opening was provided in the center of the bottom for pumping out the reaction slurry. The agitator in the tank was made of yellow pine, and consisted of a vertical shaft, 2 by 2 by 64 in., on which were mounted two horizontal paddles, which described a 43-in. diameter circle. The wood had been treated with Bakelite Resinoid BR-5995 according to the manufacturer's instruc-

The extraction charge used in the pilot plant consisted of 210 to 238 lb. of minus 100-mesh olivine and 890 to 960 lb. of 20 per cent HCl. The feed rates for the acid and olivine were adjusted so that the charge was delivered to the reaction vessel in 30 min. The feed temperature of the acid was about 70°C.; the olivine was not preheated. After about half the charge had been added, the temperature of the mixture reached boiling (110°C.). After the charge had been added, the mixture was agitated for 10 min., and magnesia (chemical grade, 93 per cent MgO) was added

TABLE 1.—*Effect of Proportion of Acid to Olivine on Extraction of Magnesium and Acid Utilization*

Number of Tests Averaged	Composition of Charge			Magnesia Required ^b (93 Per Cent MgO), Lb.	Extraction of Magnesium, Per Cent	Utilization of Acid, Per Cent		
	Acid (20 Per Cent HCl), Lb.	Olivine, Lb.	Acid Used, Per Cent of Stoichiometric ^a			MgCl ₂ from Olivine	MgCl ₂ from Magnesia	FeCl ₂ from Olivine
7	890	238	78.5	2.7	76.4	90.11	2.55	7.34
2	960	238	84.7	3.3	82.2	89.81	2.88	7.31
10	890	210	89.0	3.7	85.8	89.24	3.49	7.27
5	935	210	93.5	7.5	87.1	86.24	6.74	7.02

^a Based on MgO and FeO content of olivine.

^b For neutralization of free acid.

tions, to increase its resistance to attack by acid. The top of the shaft was held in a steel chuck connected to a motor and a speed reducer. The speed of rotation was 40 r.p.m. The reaction tank was provided with a steel cover, which was lined with Pyroflex and was fastened to the tank by means of swing bolts to facilitate replacement of the agitator. The temperature of the extraction mixture was measured by an indicating thermometer that had a 6-ft. bulb extension enclosed in a 1-in. Karbate well cemented to the brick lining. A 2-in. porcelain pipe entered the tank just below the cover and was connected with an exhaust fan for fume disposal. Olivine was charged to the tank by means of a hopper and screw feeder, and acid by gravity flow from a make-up tank through a glass plug cock and Pyrex double-pipe heat exchanger.

in amounts sufficient to combine with the free acid. Control of this operation was based on a color change of the mixture from green to gray, which occurred at a pH of about 4. Since the mixture was buffered in the range pH 4 to 5, control of this step was not difficult, although efforts were made to avoid overdosage of magnesia.

The pilot-plant extraction unit was operated for a total of 75 extractions. Operation was carried out by nontechnical personnel, and no difficulties were encountered. The wooden agitators were replaced after 30 extractions, at which time they were in a weakened condition, although none of them failed in service. The volumetric capacity required for extraction, based on the size of the pilot-plant unit, was 35 cu. ft. per ton of magnesium per 24 hr. From the standpoint of the chemistry

of the extraction procedure, there is no reason why it could not be made a continuous rather than a batch operation. Batch extraction was more convenient in the present work because of mechanical and corrosion problems, which would complicate the construction of a continuous extraction unit.

The principal variable investigated in the pilot-plant extraction was the proportion of acid to olivine. The data, averages of which are given in Table 1, show that increasing the ratio of acid to olivine from 78.5 to 89.0 per cent of stoichiometric* was desirable, since it resulted in a proportionate increase in the extraction of magnesia, from 76.4 to 85.8 per cent, without significantly affecting the amount of magnesia required for neutralization of free acid; the acid utilization by extraction of magnesia from olivine was substantially constant at about 90 per cent. A further increase in the ratio of acid to olivine to 93.5 per cent of stoichiometric was undesirable, since the magnesium extraction increased by only 1.3 per cent whereas the utilization of acid decreased by 3.0 per cent and necessitated a twofold increase in the quantity of magnesia required for neutralization of the free acid. In view of the relative costs of olivine and magnesia, it was considered desirable to use an acid-olivine ratio of about 89 per cent of stoichiometric rather than to use a higher ratio, which would require more magnesia than was justified by the improvement in extraction.

PURIFICATION

Laboratory Results

The impurities that are undesirable in magnesium chloride to be reduced to magnesium metal in electrolytic cells may be classified in two groups: (1) those that

interfere with cell operation or introduce undesirable impurities into the magnesium, such as nickel, iron, chromium, copper, boron, and sulphate and (2) those that act as diluents to the cell bath and require periodic removal; this group includes magnesia, silica, and compounds of calcium and of alkali metals. It is desirable to obtain substantially complete removal of all members of the first group. Members of the second group can be considered to be admissible in small proportions, their allowable concentration being governed by an economic balance between their removal from the magnesium chloride and replacement of the electrolyte.

Chemical and spectrographic analyses of the olivine used during the present work showed that boron, calcium, copper, and aluminum were not present in sufficient quantities to require consideration and that iron, nickel, chromium, and silica would require removal. The manganese content of the olivine was considered beneficial to the electrolytic reduction step.⁵

The purification of the mixture resulting from extraction of olivine with hydrochloric acid involved separation of the insoluble residue from the impure solution, precipitation of dissolved impurities from the solution, and separation of the precipitate from the purified solution. Unextracted olivine, silica, and most of the chromium (present as chromite) were removed in the extraction residue. The dissolved impurities consisted principally of the chlorides of iron and nickel; traces of copper and chromium may have been present. Since all the dissolved impurities form insoluble hydroxides or basic salts at a pH well below 10.5, the pH at which magnesia is precipitated,¹ their separation in this way was the obvious procedure. It was desirable to precipitate the dissolved impurities by adding a basic compound of magnesium, such as magnesium oxide or hydroxide, in order to recover the chloride ion as mag-

* Based on MgO and FeO content of olivine; Fe₂O₃ and other constituents were not considered in calculating the stoichiometric proportion of acid.

nesium chloride and to avoid the introduction of other impurities. In commercial operation, magnesia for precipitation might be prepared from a part of the magnesium chloride produced, or sludge from the electrolytic cell might be used. Cell sludge consists of a mixture of magnesia, which is formed by unavoidable decomposition of a part of the magnesium chloride during dehydration, and entrained electrolyte.

In an early stage in the development of the purification step, consideration was given to two alternative procedures: (1) a one-step procedure in which magnesia was added to the extraction slurry in sufficient quantities to precipitate the dissolved impurities, after which the extraction residue and precipitated impurities were separated from the purified solution in one operation, and (2) a two-step procedure in which the extraction residue was separated from the impure solution, magnesia was added to the clarified solution to precipitate the impurities, and the precipitate was removed from the purified solution.

When magnesia was added to the hot or cold solution after separation of the extraction residue (procedure 2), adequate purification was obtained with a small excess of magnesia. Satisfactory purification of the solution was obtained by the one-step procedure when the slurry was cooled to room temperature before addition of the magnesia; however, the one-step procedure required a larger amount of magnesia than the two-step procedure to accomplish a comparable amount of purification. When the magnesia was added to the hot slurry that contained the extraction residue, adequate purification could not be obtained, even with a large excess of magnesia. Typical data obtained in these tests are given in Table 2.

The poorer results that were obtained when the solution was purified by addition of magnesia to the extraction slurry appeared to have been caused by a tendency of the pH to decrease with time until

it reached a point at which the impurities were redissolved. This decrease in pH probably was caused by a reaction between the silica and magnesia. Since a pH of 7 or higher was necessary to ensure complete precipitation of iron and nickel, instability of the pH in this range rendered control of the operation unsatisfactory.

A further disadvantage of the one-step procedure was that magnesium oxychloride is formed² in appreciable amounts when

TABLE 2.—*Effect of Amount of Magnesia, Temperature of Solution, and Presence of Extraction Residue on Purification of Magnesium Chloride Solution**

Magnesia Added, Per Cent of Stoichiometric ^b	Solution Temperature, Deg. C.	pH of Treated Solution	Composition of Treated Solution	
			Fe	Ni
			$\frac{\text{MgCl}_2}{\times 100}$	$\frac{\text{MgCl}_2}{\times 100}$
Extraction Residue not Removed before Precipitation				
110	Room	6.7	0.22	0.013
120	Room	6.8	0.13	0.011
150	Room	7.3	0.01	<0.002
270	70	6.4	>0.10	
270	100	6.5	>0.10	
Extraction Residue Removed before Precipitation				
100	Room	7.5	0.021	
110	Room	7.3	0.012	
120	Room	7.8	0.001	<0.002
120	90	8.5	0.000	
120	108	8.0	0.001	

* Average composition of impure solutions:

$$\frac{\text{Fe}}{\text{MgCl}_2} \times 100 = 7.5; \quad \frac{\text{Ni}}{\text{MgCl}_2} \times 100 = 0.17.$$

^b Stoichiometric magnesia requirement was calculated as that required to convert all chlorides, not already present as MgCl_2 , to MgCl_2 .

magnesia is added to neutral solutions having a magnesia concentration greater than 13 per cent by weight in accordance with the following equation:



To avoid loss of magnesia by formation of this compound, it would be necessary either to use acid less concentrated than 20 per cent HCl in the extraction or to dilute the extraction slurry before adding mag-

nesia. In the two-step procedure water added for washing the extraction residue served to dilute the solution to about 13 per cent MgCl_2 . For these reasons the two-step purification procedure was considered preferable.

Several tests were made in which sludge from an experimental cell was used instead of magnesia for precipitation of iron and other dissolved impurities from solutions produced by extraction of olivine. The cell sludge contained about 25 per cent MgO ; the remainder was principally the constituents of the electrolytic bath. Analysis of the cell sludge was as follows: MgO , 24.6 per cent; MgCl_2 , 11.6; NaCl , 21.3; KCl , 21.4; BaCl_2 , 10.6. The results of these tests showed that the cell sludge was as effective as magnesia in precipitating iron and nickel from solution, per unit of MgO .

Settling tests made with the extraction slurry indicated that it would be feasible to separate the impure solution from the extraction residue by sedimentation. The applicability of continuous countercurrent decantation would depend on whether gelling occurred, as has been noted in work with similar materials containing free acid.¹² Settling tests made in the laboratory corroborated the literature. When the slurry contained free acid, gelling occurred and the residue did not settle well; when the slurry did not contain free acid, gelling did not occur and settling was satisfactory. It was concluded that the use of thickeners for separation of the extraction residue would be feasible if the free acid in the extraction slurry was neutralized. Neutralization of the free acid was accomplished by adding a small amount of magnesia as described under Extraction. This procedure had the additional advantage that acidproof materials were not required for the thickener system. A corrosion test of mild steel in extraction slurry in which the free acid had been neutralized showed a satisfactorily low penetration rate of 0.002 in. per year.

Filtration of the extraction slurry was not a promising method for separating the extraction residue because atmospheric oxidation of the solute iron caused precipitation of ferric hydroxide in the pores of the filter cloth.

Either sedimentation or filtration was found to be suitable for separation of the precipitated impurities from the purified solution. Filtration appeared to be preferable because it was more adaptable to complete removal of the precipitated impurities.

Pilot-plant Operation

Pilot-plant equipment for separating the extraction residue from the impure solution by continuous countercurrent decantation consisted of five thickeners, each with a settling area of 3.14 sq. ft. and a depth of 3 ft. They were constructed of welded, $\frac{3}{16}$ -in. mild steel. Although some contamination of the solution with iron from the thickeners was expected, this was not considered to be objectionable because the iron-removal step in the process followed the thickening step. The diaphragm pumps for the thickener sludge were steel-bodied and had ball check valves. All pumps and thickener rakes were driven from a central shaft. The piping was $\frac{3}{4}$ -in. Saran, which was used because of the ease with which large-radius bends could be made with this material. Since extraction was carried out as a batch operation, a storage tank equipped with an agitator was installed between the extraction unit and the thickeners to provide a continuous feed for the latter. The No. 1 thickener overflow constituted the clarified impure solution; it was collected in a storage tank. The No. 5 thickener underflow was discharged to waste. Repulping was obtained by converging the influent streams of sludge and solution as they entered the feed wells. The system was operated on a 24-hr. basis for a period of 6 weeks; with an average daily capacity of 700 lb. of

MgCl₂ in the form of 13 per cent solution. The thickeners operated satisfactorily, and no formation of gel was noted. Based on the size of the pilot-plant thickener system the settling area requirement would be 35 sq. ft. per thickener per ton of magnesium per day.

Impure solution from the thickener system was treated in 180-gal. batches in a steel tank equipped with a mixer by adding magnesia until the pH of the solution reached or exceeded 7. The average magnesia requirement at this point corresponded to 17 per cent of the total magnesium chloride produced. The solution containing the precipitated impurities was pumped to a cast-iron filter press having seven 12 by 12 by 2-in. frames. Eight-ounce duck covered with a layer of

most effective operation of the system and indicate that during this period 98 per cent of the residue was removed by the thickeners as underflow and that the loss of chloride in the underflow was only 2.5 per cent of the chloride input. The data given in the flowsheet (Fig. 1), which are based on an average of the 6-week period of operation, indicate that about 3.8 per cent of the total chloride input was lost in the underflow.

The magnesia requirement for precipitation of metallic impurities from the clarified solution in the pilot plant was about 250 per cent of stoichiometric,

TABLE 3.—Analysis and Flows of Thickener Feed, Overflow, and Underflow

	Grams per Liter					Specific Gravity	Flow Rates, Gal. per Hr.
	Mg ⁺⁺	Cl ⁻	Fe ⁺⁺	Fe ⁺⁺⁺	Insolubles ^a		
Feed...	60.4	198.8	12.0	0.04	144.9	1.297	12.5
Over-flow.	37.4	113.6	6.2	0.01	1.6	1.127	22.5
Under-flow. Water.	2.5	7.2	0.3	0.00	184.2	1.115	8.5 18.6

^a Dried at 110°C.

30-lb. or 40-lb. Kraft paper or newsprint was found to be a satisfactory filter medium. The filter pressure was from 5 to 25 lb. per sq. in., with an average filtration rate of 0.43 gal. per sq. ft. per min. Although the filter press was a nonwashing type, a certain degree of washing was obtained by following each batch with 16 gal. of water. Based on the size of the pilot-plant filter, the filter requirement for the process would be 42 sq. ft. of filter area per ton of magnesium per 24 hours.

Data showing the flow rates and chemical composition of the feed, overflow, and underflow from the thickener system are given in Table 3. These data represent the

TABLE 4.—Composition of Materials from the Precipitation Step

Filter Cake		Purified Solution	
Constituent	Per Cent by Weight	Constituent	Per Cent by Weight, MgCl ₂ Basis
Mg(OH) ₂	8.4	Fe	0.012
Fe(OH) ₂	10.6	Ni	0.000
Fe(OH) ₃	7.1	Mn	0.025
Ni(OH) ₂	0.78	Cr	0.000
SiO ₂	9.0	SiO ₂	0.004
MgCl ₂	3.5	SO ₄	0.107
Moisture....	52.1 ^a	Ca	0.000

^a Loss on drying at 110°C.

although small-scale tests (Table 2) had indicated that 120 per cent of stoichiometric was sufficient when no silica was present in the solution. The increased magnesia requirement in the pilot plant was attributed to the presence of silica in the clarified solution from the thickeners as shown by the analysis of the filter cake (Table 4). It is believed that the magnesia requirement can be decreased by better operation of the thickeners or by filtration of the thickener overflow for removal of silica.

The amounts of impurities in the purified solution were believed to be sufficiently low for production of a satisfactory magnesium chloride cell feed, with the possible exception of the sulphate content. Since the presence of sulphate was not suspected,

no provision was made for its removal, which presumably can be accomplished by addition of a small amount of barium chloride during the precipitation step. Barium chloride is not an objectionable impurity in magnesium chloride cell feed.⁴

A material balance over the extraction and purification steps of the pilot plant for the 6-week period of operation covered by this paper is represented by the data in the flowsheet (Fig. 1). The magnesium distribution in the system is shown in Table 5. These data indicate that 76.5

TABLE 5.—*Magnesium Distribution in Extraction and Purification Steps*
PER CENT

Input		Output	
Olivine.....	84.1	Unextracted olivine in sludge.....	11.8
Magnesia (to extraction step)...	2.7	MgCl ₂ in thickener underflow.....	2.7
Magnesia (to purification step)....	13.2	Mg(OH) ₂ in filter cake.....	7.7
Total.....	100.0	MgCl ₂ in filter cake.....	1.3
		MgCl ₂ in purified solution.....	76.5
		Total.....	100.0

per cent of the total magnesia added was recovered as magnesium chloride in the purified solution.

If it were assumed that the magnesia added to the extraction and purification steps was obtained by recycling material produced from magnesium chloride in a later step, such as cell sludge or magnesia obtained by hydrolysis of magnesium chloride, the net recovery of magnesia from olivine would be 72.1 per cent. The magnesia recycled would amount to 20.8 per cent of the total magnesium chloride produced. The recovery of chlorine in the purified magnesium chloride solution was 94.7 per cent of the chlorine input as hydrochloric acid. These results are an average of those obtained in operation of the pilot plant under various conditions, some of which were known to be unfavorable to high recovery. Various means by which it is expected that the recoveries

can be improved have been pointed out in the previous discussion.

STEPS COMMON TO OTHER ELECTROLYTIC MAGNESIUM PROCESSES

Other steps of the process were common to other processes for the production of electrolytic magnesium. These steps were included in the pilot plant in order to complete the cycle of the process and to supplement the information available in the literature. For this reason, and because complete data have not yet been obtained in some units of the pilot plant, these steps will be described only briefly.

Evaporating and Flaking.—Purified magnesium chloride solution was evaporated in an open-top, brick-lined, steel tank equipped with stainless-steel steam tubes. After the concentration of the solution reached 48 per cent MgCl₂, the hot solution was run from the evaporator to a water-cooled drum flaker, which produced magnesium chloride flake of approximately hexahydrate composition.

Drying.—The flake chloride was dried in a rotary drier, fired with by-product carbon monoxide gas, to a composition that corresponded to the dihydrate.

Electrolytic Reduction.—Electrolysis of magnesium chloride was carried out in a 4000-amp. cell of conventional design. The cell gases were sent to the acid-manufacturing unit for recovery as hydrochloric acid.

Acid Manufacture.—Hydrochloric acid was manufactured from chlorine, coke, and steam by the reaction:



The equipment consisted of a shaft furnace, in which the reaction was carried out, a gas cooler, an absorber, and a storage tank. The capacity was about 1.2 tons of 20 per cent acid per 24 hr. Commercial chlorine was used in most of the pilot-plant operation described in this paper. During the latter part of the investigation,

when the electrolytic cell was being operated, cell gas was used as a source of acid.

CONCLUSIONS

The results of this investigation show that it is technically feasible to produce from olivine magnesium chloride believed to be of satisfactory purity for electrolytic production of magnesium, and that all steps of the process can be carried out with relatively simple equipment. The cost of producing magnesium chloride represents a relatively small part of the production cost of electrolytic magnesium; therefore economies in magnesium chloride production can have but small influence on over-all costs. However, the process would have important economic advantages because of the use of olivine as a raw material. These advantages may be listed as follows:

1. The geographic location of the olivine deposits is favorable because of the availability of large quantities of hydroelectric power. The location is also favorable with respect to markets, since a considerable portion of the aluminum industry, which uses large quantities of magnesium for production of alloys, is in the Tennessee Valley.

2. The magnitude and uniformity of any one of several olivine deposits in the Tennessee Valley region would ensure a supply of raw material for operation of a magnesium reduction plant for a period of time sufficient for amortization of the large capital investment required for electrolytic magnesium production.

3. The high magnesium content and high specific gravity of the olivine would favor low transportation costs per unit of magnesium and should allow considerable latitude in selecting a plant location to utilize existing electric power transmission and rail transportation facilities.

4. The possibility of by-product recovery is favorable. Although the olivine used in the experimental work was low in

chromite, it would be feasible to use olivine containing several per cent of chromite.⁷ Previous attempts to produce chromite from these deposits were not economically successful because the value of the chromite was insufficient to bear the costs of quarrying and crushing the olivine. If these costs were chargeable to magnesium production, there is little doubt that chromite recovery would be profitable. The feasibility of nickel recovery was not investigated; however, it is believed that a feasible process for extraction of the nickel from the filter cake could be developed.

Since the process described in this paper permits utilization of the economic advantages enumerated above, it is concluded that the production of magnesium from olivine warrants consideration in postwar industrial planning. Olivine was selected for this study in preference to serpentine because of the superior quantity and uniformity of the deposits of olivine in the Tennessee Valley. However, the two minerals are closely related in composition, chemical properties, and mineralogy, and tests have indicated that the process probably is applicable to serpentine as well as to olivine.

ACKNOWLEDGMENTS

Appreciation is expressed for the cooperation received from the staff of the Georgia State Engineering Experiment Station in providing facilities and equipment for intermediate-scale investigation of the process. The author is indebted to G. H. Montillon and H. S. Rankin, of the Tennessee Valley Authority Commerce Department, for information, assistance, and encouragement. Acknowledgment is made to R. L. Copson and J. H. Walthall, for helpful criticism and advice and to L. D. Yates, G. C. Robinson, H. J. Kerr, and other engineers who participated in the experimental program at Wilson Dam. T. P. Hignett assisted in the preparation of this paper.

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The Mufulira Smelter, Northern Rhodesia

By F. E. BUCH*

INTRODUCTION

THE Smelter is designed for a production capacity of 10,000 short tons of blister copper per month, when operating on the present concentrate grade.

The Smelter lay-out is shown in Fig 1.

The major units of equipment comprise two reverberatory furnaces, three 13 by 30 ft Peirce-Smith converters, two straight line casting machines, one being served by a 13 by 30 ft holding furnace and the other by a ladle tilting quadrant, two converter aisle cranes and two converter blowers.

The plant is compact and the general arrangement of standard gauge railway tracks and conveyor belts provides for a smooth flow of incoming materials and metallurgical products. Concentrate is received by conveyor belts and fluxes in standard railway trucks. The local track system is covered by an electric trolley locomotive.

The Smelter treats a wet (10 pct moisture) flotation concentrate containing approximately 33 pct total copper and 0.9 pct oxide copper.

The predominating minerals are chalcocite, chalcopyrite and bornite accompanied by small quantities of malachite and cuprite. The gangue is highly siliceous and requires limerock as a flux.

Metallurgy would be straightforward were it not for the necessity for eliminating bismuth which occurs as an impurity in the ore along with the copper. Directly

or indirectly most of the Smelter problems can be traced to the necessity for bismuth removal.

Copper recovery, based on new copper treated, averages 97.5 pct.

GENERAL DESCRIPTION

Flotation concentrate, containing 10 pct moisture, is conveyed from the filter plant to the smelter storage bins by conveyor belts, the material being weighed in transit by a revolving drum type of weigh-hopper manufactured by Samuel Denison and Son, Ltd. The weigher consists of a steel drum with dished ends carried on a horizontal shaft and rotated by an 8 hp squirrel-cage motor through a worm and spur reduction gear. A feed mouth in the drum permits of filling and discharging.

The whole unit is supported on a framework resting on weighing levers, which in turn connect to transfer levers, thence to an indicator of the steelyard type situated 16 ft from the centre line of the drum. The indicator is of the "Denison" patent equilibrium controlled ticket stamping type, insuring mistake-proof records by a combination of electrical and mechanical movements which prevent the operator from printing until the cover enclosing the steelyard is closed and until the poise-weights have been set correctly to the weight of the hopper and contents.

The machine is capable of weighing 30 short tons at a time but the usual load is 28 tons. After obtaining the gross weight the drum is rotated and discharged into a receiving bin situated below it. The empty drum is weighed and the net weight re-

Manuscript received at the office of the Institute April 19, 1947. Issued as TP 2248 in METALS TECHNOLOGY, December 1947.

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feeder which delivers to a 30 in. belt feeding the flux-crushing plant.

The flux-crushing plant consists of one 36 by 24 in. and one 24 by 15 in. Allis-

Reverberatory Section

The two reverberatory furnaces are each 100 ft 6 in. long by 28 ft wide by 11 ft 6 in. high, internal dimensions. The side



FIG 2—GENERAL VIEW OF SMELTER.

Chalmers jaw crusher, both of the Blake type, and one 5½ ft Symons shorthead cone crusher in series. Crushed material is conveyed by belts to the charge bins and distributed by means of a travelling tripper.

walls, which are 2 ft thick are built mainly of high-alumina brick, which in the settling zone is faced with magnesite brick to bath level and with chrome-magnesite above bath level. The burner and up-take walls are built with magnesite brick. Until June

TABLE 1—Operating Data. Treatment and Production for the 6 Years July 1939 to June 1945
Data expressed in short tons

	1939-40	1940-41	1941-42	1942-43	1943-44	1944-45
Concentrate smelted.....	156,920	175,907	182,010	172,148	150,230	120,715
Dry solid charge smelted.....	194,047	227,047	257,043	231,082	211,029	176,666
Furnace days operating.....	508	666	603	695	507	357
Dry solid charge per furnace day.....	383	342	420	332	416	495
Reverberatory fuel per furnace day (as received).....	75.5	67.8	73.7	63.1	74.6	83.5
Reverberatory fuel per cent of dry solid charge (coal as received).....	19.7	19.8	17.3	19.0	17.9	16.9
Millions B.T.U. (gross) per ton dry solid charge.....	5.12	5.15	4.49	4.94	4.65	4.39
Reverberatory slag to dump.....	55,255	67,367	80,042	72,802	68,008	55,424
Flux ore to converters.....	477	920	4,840	4,700	5,424	4,776
Blister copper produced.....	79,851	88,705*	86,678*	89,181*	79,439*	64,442

* Mine production was actually higher than this as some ore and concentrate were smelted elsewhere. Peak production was in July 1940 when the Smelter turned out 9200 short tons blister copper.

Limerock and iron pyrites are crushed to ½ in. size, and reverts, which are not sent through the Symons crusher, to about 2½ in.

1944, the roof, which is of suspended type construction, was built with either silica or high-alumina brick in 20 × 12 × 3 in. tiles. Burnt chrome-magnesite in 15 × 6 ×



FIG 3—REVERBERATORY FURNACE SHOWING BURNERS.



FIG 4—SKIMMING REVERBERATORY SLAG.

3 in. size has now replaced silica and high-alumina, and the indications are that roof life will probably be doubled.

In both furnaces, the working bottoms are of reverberatory slag. In No. 1 the bottom was made by charging crushed slag and melting it with pulverised coal through the furnace burners. The thickness of the working bottom is about 5 ft. The slag for No. 1 bottom was obtained from the Nkana smelter slag dump and crushed to $\frac{1}{2}$ in. ring before being charged. The working bottom for No. 2 Reverberatory was poured by laundering slag from the skimming bay of No. 1 Reverberatory through a hole in the side wall of No. 2. The furnace was kept hot by burning pulverised coal throughout the whole of the pouring period. In each case after the desired thickness of working bottom had been attained, the coal was cut off and the furnace well sealed and allowed to cool down very slowly. Working bottoms thus constructed have proved very satisfactory.

The two furnaces are provided with three tunnels so that matte and slag can be tapped and skimmed at either side of each furnace. The skimming bays are situated 85 ft and the tapholes 78 ft from the burner walls. Each furnace is equipped with 6 burners for pulverised coal. Coal for No. 1 Reverberatory is pulverized in two No. 80 Impax pulverisers, and that for No. 2 Reverberatory in two No. 8 Fuller Bonnot Ball mills. Each grinding unit has a capacity of 80 tons per day, at a fineness of 80 pct minus 200 mesh. The pulverized coal is transported by fans straight from the mills to the furnace burners. Normally on each furnace one mill supplies the 4 centre burners and the other the 2 outside burners.

Hot secondary air for combustion is supplied to each furnace through a lagged, 4 ft 9 in. diameter conduit from the air pre-heater. No. 1 Reverberatory has two secondary air fans each capable of delivering 21,600 cfm at 82°F, whereas No. 2

Reverberatory has one fan capable of delivering 42,000 cfm at 82°F.

The coal for combustion is obtained from Wankie colliery in Southern Rhodesia and is a bituminous type of excellent quality and of the following composition:

	PER CENT
Carbon (total).....	77.1
Hydrogen.....	4.3
Oxygen.....	4.3
Nitrogen.....	1.6
Sulphur.....	1.4
Moisture.....	1.2
Ash.....	10.1
Volatile matter.....	26.0
Calorific value.....	13250 B.T.U. per lb

After leaving the furnace, the products of combustion pass through a 60,000 lb per hour Class 12 Stirling water tube boiler, there being one for each furnace. The boiler produces steam at 275 psi pressure and total temperature of 655°F. The temperature of the feed water is 170°F.

The boiler heating surface has an area of 13,045 sq ft, made up as follows:

	Sq Ft
Boiler.....	11,250
Front water screen.....	920
Bailey walls.....	875

The gases from the boiler pass through a plate type air preheater, capable of handling 176,500 lb of gas and 126,000 lb of air per hr. The gas temperature drops from 650 to 400°F and the air is heated from approximately 80 to 400°F.

In the case of No. 1 Reverberatory the gases leaving the preheater are handled by two induced draught fans, each of 46,000 cfm capacity at 380°F, which deliver the gases into a baffled brick dust settling chamber of 410 sq ft cross-section and 55 ft length, and then up the main stack. The stack is 210 ft high and is a brick-lined steel structure of 12 ft 2 in. diam inside the brickwork.

The gases leaving No. 2 Reverberatory preheater enter an Edgar-Allen-Buell, 10 cyclone, "Microlector" flue dust collector, which is capable of dealing with 95,000 cfm of gas at 500°F at a resistance of 2 in.

water gauge. The plant is guaranteed to give the following dust recovery:

PER CENT

98	of all dust particles of 20 micron size
97	of all dust particles of 15 micron size
96	of all dust particles of 10 micron size
93	of all dust particles of 8 micron size
90	of all dust particles of 7 micron size

which are hauled along the matte tunnels by electrically driven winches. Four ladles totalling approximately 80 tons constitute a normal converter charge.

Slag is skimmed into cast iron pots of 200 cu ft capacity carried on bogies incor-

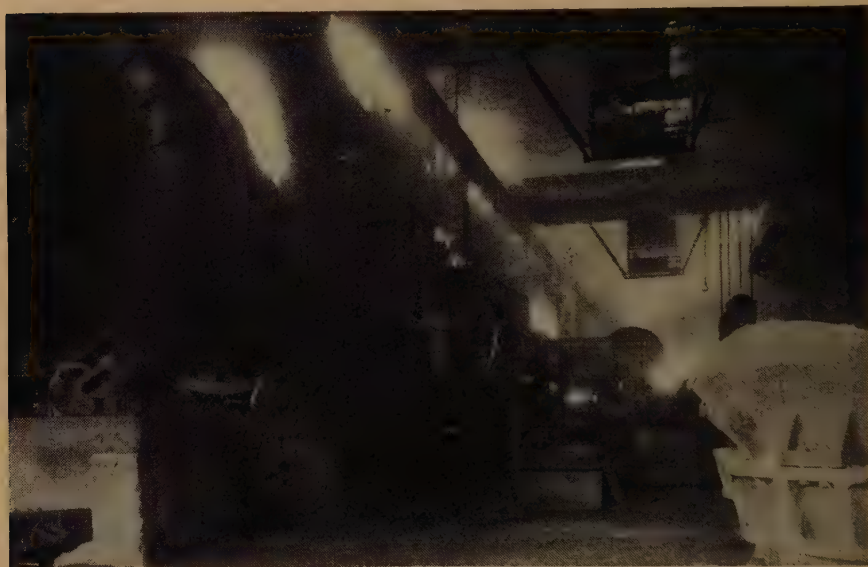


FIG 5—VIEW OF CONVERTER AISLE.

Approximately 48 pct of the dust collected by this plant is less than 10 microns in size. A connecting duct between the two reverberatories makes the "Microlector" available for use with either furnace. Gases leaving the "Microlector" are sent up the stack by one induced draught fan of 92,000 cfm capacity at 380°F.

Flue dust collected by the "Microlector" system is conveyed by means of a bucket elevator and screw conveyors to a surge bin of 13 tons capacity situated at the tail end of the central conveyor belt running under the charge bins. A screw feeder, electrically interlocked with the charge bin feeder system, delivers flue dust from the surge bin to the central belt when normal charge is being conveyed to the furnaces.

Matte is tapped into 150 cu ft capacity cast steel ladles carried on low slung bogies

porating an electrically-operated tipping mechanism. The train of pots is hauled by a 20 ton Jeffrey trolley locomotive, the controller for the tipping mechanism being in the driver's cab. The slag dump is 500 yd from the smelter.

The reverberatories are side charged through 8 in. diam pipes spaced at 5 ft intervals, there being 14 pipes on each side. Converter slag is received through a cast iron launder which enters the top of the burner wall on the furnace centerline. Clay for tap-hole stoppers, skimming bay breasts, and others, is ground in a Bradley and Craven 7 ft solid bottom wet pan mill.

Converter Section

The converter aisle is 300 ft long and accommodates the converters, holding furnace, casting machines and overhead

cranes. The three 13 by 30 ft Peirce-Smith converters are lined with magnesite brick throughout. The converter has 45 tuyeres of $1\frac{1}{2}$ in. diam spaced at 6 in. centres.

a gauge pressure of 15 psi. The blowers are situated in the power plant.

Coal for the converters and holding furnace is pulverized by a No. 70 Impax pul-



FIG 6—CHARGING HOLDING FURNACE.

Gases from each converter pass through a steel dust settling flue of 170 sq ft cross-section and 60 ft length, surmounted by a 65 by 6 ft diam unlined steel stack.

The converters are rotated by twin 35 hp Holman air motors through reduction gearing. Compressed air for operating the motors is supplied at 80 lb pressure, and is stored in a receiver provided with a nonreturn valve. There is at all times sufficient air in the receiver to turn the tuyeres out of the bath in the event of a sudden electrical power failure while blowing.

Air for blowing is supplied by two Bellis-Reavell steam turbo-blowers each having a capacity of 20,000 cfm of free air and capable of delivering this volume against

verizer in closed circuit with a cyclone. The pulverized coal is distributed to storage bins by a 4 in. Fuller-Kinyon pump of 2 tons per hr capacity.

Casting Section

Casting equipment consists of two straight-line casting machines, one being served by a holding furnace and the other by a ladle tilting quadrant. The pulverized coal-fired, cylindrical, 13 by 30 ft holding furnace is lined with magnesite brick backed by a 3 in. course of insulating brick. The furnace is rotated by a 50 hp motor through reduction gearing. No. 1 casting machine, served by the holding furnace, has 60 copper molds bolted to an

endless chain carried on head and tail sprockets, and driven by a 20 hp reversing type motor through reduction gearing. The molds, each weighing 1200 lb, are cast

TABLE 2—*Typical Recent Converter Data*

Tons matte per blow.....	76.5
Tons copper scrap re-melted per blow...	6
Tons reverberatory slag as flux per blow	10
Tons Mufulira ore as flux per blow....	4
Tons blister produced per blow.....	47.5
Minutes blowing time per blow.....	198
Minutes blowing time per ton matte...	2.59
Minutes blowing time per ton blister...	4.17
Tons blister copper per converter hour.	14.4
Average blower air pressure.....	13 psi

of clear copper in cast iron molds and each has embedded in the bottom a cast iron pouring plate.

The blister copper cakes which measure 27 by 17 by 4 in. thick and weigh about 375 lb each are quenched by water sprays soon after being cast and are then delivered to a slow moving finning conveyor where they are inspected and trimmed for shipment.

The design of No. 2 casting machine, served by a ladle tilting quadrant, is identical with that of No. 1, except that it has 50 molds instead of 60.

The holding furnace is normally operated, the tilting quadrant being used as a standby.

The converter aisle is served by two overhead cranes each having a span of 57 ft 6 in. They are of the 5-motor type with independently operated main and auxiliary hoists, the former having a lifting capacity of 50 tons and the latter of 20 tons.

METALLURGY

Reverberatory furnace metallurgy is directed at producing a satisfactory slag and matte of a grade suitable for the desired degree of bismuth elimination in the converters. The theories and technique of bismuth elimination are dealt with at a later stage in this paper.

As the concentrate is deficient in bases, limerock flux is used to produce a slag having a silicate degree between 1.20 and 1.30. The limerock consumed is approxi-

mately 12.5 pct of the concentrate charged.

Concentrate approximating the analysis given in Table 3 will smelt to a matte containing about 64.2 pct Cu. This is too high a grade for the required degree of bismuth elimination and iron pyrites is added to the furnace charge to lower the grade to about 61 pct Cu. Pyrite consumption has recently averaged 5.8 pct of concentrate smelted.

In order to conserve as much of the sulphur as possible, the furnace is run with a reducing atmosphere and in addition "duff" coal (all $\frac{1}{4}$ in. size) is mixed with the charge as a reducing agent. Coal addition averages 1.6 pct of concentrate smelted.

At one time the pyrite and coal requirements were obtained in the form of coal "dross," a coal washery reject, which contained $\frac{1}{3}$ iron pyrites, $\frac{1}{3}$ coal and $\frac{1}{3}$ shale. "Dross" was added at the concentrator to the mill feed. Most of the coal and pyrite was floated with the concentrate and most of the shale eliminated with the tailings. This method worked very well as long as the pyrite content of the "dross" remained reasonably high. A drop in the pyrite content was usually accompanied by an increase in coal. For the first few years of its use the pyrite grade of the material remained fairly high, at times rising to 45 pct, but after that the grade dropped to 20 pct pyrite accompanied by 60 pct coal. In order to obtain the necessary iron sulphide, more "dross" had to be added and this resulted in an excessive amount of coal entering the furnace with the charge.

The coal, which at times was as high as 8.5 pct of the concentrate was responsible for considerably impaired furnace efficiency and reduced refractory life. Concentrate containing 10 pct moisture does dust to some extent in the furnace, but when mixed with a large amount of coal, dusting is very severe. Inspection of the charge piles reveals a large number of small volcanic-like

eruptions, each little crater burning with a small blue carbon monoxide flame. The eruptions are most probably caused by the

rapid choking of the boiler tubes and consequent loss in furnace draught.

In spite of almost continuous air-lancing



FIG 7—TRIMMING BLISTER COPPER. CASTING MACHINE IN BACKGROUND.

distilled volatile matter of the coal bursting through the fused skin of the charge pile, and each little explosion shoots dust up into

of the boiler tubes, draught was lost so rapidly that six months after the start of a new furnace campaign it was barely pos-

TABLE 3—Recent Average Analyses—Per Cent

	Total Cu	Oxide Cu	Fe	S	SiO ₂	FeO	CaO	Al ₂ O ₃	MgO	Silicate Degree
Concentrate.....	52.80	0.85	9.8	20.8	11.8		0.4	2.0	0.4	
Matte.....	61.10		14.3	23.4						
Reverberatory slag.....	0.57			0.3	37.7	33.7	15.0	6.7	1.3	1.30
Converter slag.....	9.84			2.8	21.5	51.7	6.5	3.5	1.0	
Reverberatory flue dust.....	36.71			4.3						
Converter flue dust.....	78.77			9.8						
Reverts.....	15.95			3.5						
Coal ash.....					41.0	8.0	8.8	36.3	1.0	
Limerock.....							51.7			
Iron pyrites.....			38.1	40.6						
Flux ore.....	3.25	0.18	1.7	1.2	74.0		3.0	8.6	2.2	
Blister copper.....	99.50									

the gas stream. Under these conditions large quantities of dust and partially burnt coal enter the waste heat boiler causing

sible to burn 75 tons of coal per day. Fuel efficiency and furnace capacity naturally suffered, and the position was aggravated

by having only one waste heat boiler per furnace. The furnace brickwork was subjected to the erosive action of the dust and refractory life was further shortened by the necessity of maintaining a reducing atmosphere.

At the end of 1940 it was decided to replace a portion of the "dross" by iron pyrites obtained from Southern Rhodesia, and added to the furnace charge at the Smelter. The addition of pyrite was progressively increased and that of "dross" diminished until in January 1944 the use of "dross" was discontinued.

The reduction of coal (which is also added in the Smelter) to 1.6 pct of concentrate resulted almost immediately in improved fuel efficiency, longer refractory life and less choking of the boiler tubes. In the last campaign of No. 1 Reverberatory it was still possible to burn 90 tons of coal per day after 13 months continuous operating. The necessity for maintaining a reducing atmosphere results in rather poorer fuel ratios than might otherwise be obtained, and although the longer burner flame is balanced by increased waste heat steam return, the function of a reverberatory furnace is to smelt charge and not to produce steam.

The heat balance for the reverberatory furnaces for the past 18 months has been estimated as follows:

	PER CENT
Heat input	
Burner coal.....	93.7
Duff coal.....	6.3
	100.0
Heat output	
Slag.....	8.5
Matte.....	12.0
Limerock decomposition.....	2.7
Waste heat steam.....	54.4
Waste gases.....	10.7
Radiation, conduction, etc., losses.....	11.7
	100.0

Furnace draught is maintained at 0.020 in. of water, measured through a hole in the roof 75 ft from the burner wall.

When the Smelter first started operations the composition of the concentrate was

such as to give matte grades running up to 75 pct Cu, but the iron sulphide content of the concentrate has steadily increased throughout the years until at present a matte grade of 64 pct Cu can be produced without the use of extraneous pyrite.

Depending upon the required bismuth content of the final blister, mattes varying from 59 to 75 pct Cu have been treated. Mattes running over 70 pct Cu are unwellcome from the point of view of both furnace and converter operations. This very high grade matte does not flow freely from the taphole and causes considerable launder cleanings and thick ladle skulls, and in addition means increased oxygen and pipe consumption in burning open the taphole. Furthermore, matte of this grade seems to have very little solvent power for any metallic copper formed from the oxides in the concentrate, the smelting of copper bearing reverts and oxidised smelter flue dusts and the furnace tends to run a "cold bottom."

Bottom buildup troubles generally, and these includes magnetite deposition, are encountered to some extent with all matte grades down to 64 pct Cu. Below this figure, provided the furnace is run at a reasonably high temperature, bottom troubles are reduced to a minimum.

The converting of mattes running over 70 pct Cu means hard punching, cold blows and difficult fluxing. The temperature and iron content is too low for efficient silica fluxing, and the usual procedure therefore is to add about 5 tons of molten reverberatory slag to act as a scavenger for the oxidised iron.

The present practice in converting an 80 ton charge of a 61 pct Cu matte is to add 4 tons of silica flux (Mufulira ore) and ten tons of reverberatory slag to swell the converter slag volume. This is deliberate under-fluxing, the reason for which is explained in the section on bismuth elimination.

The converter charge is blown to a

medium blister, the finishing point being determined by inspection of punch-rod samples.

BISMUTH ELIMINATION

In order to make the product acceptable to fire-refiners in Great Britain, the Smelter is required to produce blister copper having a bismuth content of less than 0.0025 pct.

Stated briefly, the degree of bismuth elimination in the converter is a function of temperature and delayed copper formation. The lower the grade of matte the higher is the temperature developed and the longer the blowing time to the "white metal" (Cu_2S) stage, due to the increased amount of iron which has to be oxidized and slagged. Therefore the lower the grade of matte the higher is the degree of bismuth elimination. Bismuth thus appears to be eliminated by fuming accelerated by the agitating action of the air streams through the molten matte bath. Elimination continues until sufficient metallic copper is formed to act as an avid collector of bismuth, at which point elimination ceases.

The rules for achieving maximum bismuth removal at any particular matte grade may be summarized as follows:

1. The converter must be kept hot between blows. This is done by burning pulverized coal at the rate of 850 lb per hr through a port in one of the end walls, the lining being maintained at a surface temperature of approximately 2100°F .

2. The addition of cold material, which would lower the bath temperature, must be limited. This means underfluxing with cold silica flux.

3. Cold copper scrap must not be added until bismuth elimination has ceased. This point is determined in practice by the first appearance of a copper coating on the punch-rods.

4. The converter must be drained thoroughly of copper and residual slag (which retains some copper) at the end of each

blow. This results in increased converter aisle reverts.

The high temperature (over 2400°F) maintained for the first half of the blow and the preclusion of adding cold "dope" until the peak temperature has been passed inevitably results in increased converter refractories consumption. It is exceedingly difficult to maintain a protective magnetite lining, and tuyere line life is of the order of 5000 tons of copper.

The following figures show the degree of bismuth removal actually achieved:

	Pct Cu	Pct Bi	Lb Bi per ton Cu
Concentrate.....	52.80	0.030	1.136
Matte.....	61.10	0.022	0.720
Blister copper.....	99.50	0.0018	0.036

	PER CENT
Reverberatory elimination from concentrate.....	36.6
Converter elimination from matte.....	95.0
Overall Smelter elimination.....	96.8

As yet no method has been devised to improve reverberatory elimination, bar the withdrawal of flue dust, (which contains about 0.2 pct condensed bismuth oxide fume), from the furnace circuit.

The graph in figure 8 shows the relationship between the degree of bismuth elimination in the converter and the grade of matte. It will be observed that the curve flattens out at the lower matte grades and very little improvement in elimination is obtained by lowering the grade below 60 pct Cu.

The reasons for this phenomenon are probably as follows: 1. Matte always contains some metallic copper which limits the degree of bismuth removal which can be achieved and 2. The lower grades of matte require more cold flux for reasonably efficient blowing and this nullifies to some extent the heat benefit from lowering the matte grade.

Very recently the writer has carried the temperature side of bismuth removal a stage further by burning pulverized coal

in the converter, at the rate of 1300 lb per hr, for the first 30 to 45 min of the blow. The increase in temperature is marked and the improvement in bismuth removal immediate. By this method it is now possible

tions and 2. "Splash shot" sampling for impurity determinations.

In drill sampling, 8 cakes are selected at definite intervals from every 40 to 45 ton lot during casting operations.



FIG 8—RELATIONSHIP BETWEEN DEGREE OF BISMUTH ELIMINATION IN CONVERTER AND GRADE OF MATTE.

to treat a 63 pct Cu matte and eliminate to a 0.0017 pct blister bismuth, with a consequent considerable saving in iron pyrites consumption.

Great credit is due to the Smelter organization of Roan Antelope Copper Mines,

One $\frac{5}{8}$ in. diam hole is drilled half-way through each cake. Half the cakes are drilled from the blister side and half from the mold side. The location of the drill hole is varied from cake to cake. The drillings from the 8 cakes are combined and sent

TABLE 4—Recent Average Impurities Analyses—Per Cent

	Pb	Fe	S	Bi	As	Sb	Ni	Co	Se	Te
Concentrate....				0.030	0.0026	0.0008	0.0033			
Matte.....				0.022	0.0039		0.0080			
Iron pyrites....				Trace	0.0025	0.0008	0.0058			
Blister copper...	0.0012	0.011	0.066	0.0018	0.0012	0.0003	0.0062	Trace	0.0017	0.0001

Ltd., for working out the successful bismuth elimination technique, and when the Mufulira Smelter started operations it had the benefit of Roan's experience.

BLISTER COPPER SAMPLING

Two methods of sampling are practiced:

1 Drill sampling for fine copper determina-

to the laboratory for preparation and analysis.

The above method is considered suitable for samples on which fine copper is to be determined but not suitable for bismuth determinations because of the segregation of this impurity in the copper cake. Bismuth concentrations at the blister surface have

been found to be three times that at the bottom or mold side.

Unless careful template drilling is resorted to, drill samples will not give representative bismuth assays.

In "splash shot" sampling a strong water jet is directed through the stream of copper as it issues from the holding furnace, and the shot thus formed collected in a drum of water. Spraying is done at frequent intervals throughout the cast. The sample for each lot of 40-45 tons of copper is screened on 4-mesh to remove the large pieces and the balance sent to the laboratory for preparation and analysis.

This method of sampling overcomes segregation difficulties, and it is considered

that shot samples give representative bismuth assays.

The chemical laboratory, under Smelter control, is modern, well equipped and staffed by qualified chemists carrying out investigation work as well as the routine analyses of mine, concentrator and smelter samples.

PERSONNEL

The ratio of native to European labor is approximately 10 to 1. Most of the Europeans have received their training on the copperbelt. Natives show remarkable adaptability to smelter work and soon become proficient at routine jobs not requiring too much personal judgment.

Roan Antelope Smelter, Northern Rhodesia

By R. J. STEVENS,* JUNIOR MEMBER AIME

(New York Meeting, February 1948)

THE Roan Antelope Smelter commenced operations in October, 1931. As originally designed, its equipment consisted of one reverberatory furnace, 120 × 25 ft, two Peirce-Smith converters 12 × 20 ft, and one straight line casting machine. Since that time the following additions have been made:

One reverberatory furnace 120 ft
× 28 ft (1934)
One reverberatory furnace 95 ft
× 28 ft (1943)
Two 12 × 20 ft Peirce-Smith
converters (1934 and 1938)
One 13 × 30 ft holding furnace (1938)
One straight line casting machine
and 2 ladle tilting quadrants (1934)

The metallurgy of the smelting process is comparatively simple. However, there are several features of operation which are uncommon to most copper smelters: (1) The high grade of concentrate treated; this has always been about 50 pct copper. (2) The high flux burden on the charge. This is necessary because of the deficiency of bases in the concentrate and the high alumina content of the concentrate. (3) The frequent necessity of adding coal to the furnace charge to control the matte grade. (4) The high grade of matte produced. This has led to unusual converter problems.

From the commencement of operations, the ore mined has come from the Roan Basin orebody. The concentrate produced

from this ore consists mainly of chalcocite and shale with small proportions of other copper minerals. As mining operations extend to the Roan Extension orebody, the proportions of bornite and chalcopyrite in the concentrate will increase with a corresponding decrease in the copper content of the concentrate. Because of the concentrate grade the capacity of the reverberatory furnaces in terms of tons of copper produced per ton of coal burned is high. This ratio is usually over 2.2, and on especially favourable runs has reached 2.6.

Reference to Table 1 shows that the iron content of the concentrate is unusually low. Only part of this iron is available for slag formation, the balance going to the matte. To make up this deficiency in bases, limerock is added to the furnace charge. This flux ensures a slag that is of the correct silicate degree, is sufficiently fluid, of low specific gravity, and it counteracts the thickening effect of the alumina present. An ample supply of flux is obtainable from Ndola, 22 miles distant by rail. Although the reverberatory slag has a high copper content, the slag fall is low and the copper loss in the slag now rarely exceeds 1.0 pct of the total copper charged.

The blister copper shipped is of such purity that only one fire refining operation has been necessary to produce a wirebar with properties comparable to electrolytic copper. Bismuth has always been the most troublesome impurity and consequently the problem of its control in the finished product has been of prime importance. Practically none is removed in the reverberatory furnace. The bulk of the elimina-

Manuscript received at the office of the Institute April 19, 1947. Issued as TP 2249 in METALS TECHNOLOGY, December 1947.

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tion is accomplished in the converters. It was established in 1934 that this removal was, generally speaking, inversely proportional to the grade of matte. Whether this

atmosphere in the furnace, the degree of oxidation of iron sulphide is minimized and a lower grade matte results. The effect of coal in reducing the grade is limited;



FIG 1—GENERAL VIEW OF SMELTER. TAILINGS DAM IN BACKGROUND. POWER STATION IN RIGHT FOREGROUND.

is due to longer blowing time or to the higher temperature attainable with a lower grade of matte is not clear, although current opinion tends to favor the latter view.

when more than 3 pct of coal is added to the total solid charge no further lowering of matte grade is achieved. It becomes mandatory to charge barren iron pyrites

TABLE I—*Reverberatory Assays*
By Percentage

Year Ending June 30	Concentrate							Matte			Reverberatory Slag						
	Cu	SiO ₂	FeO	Al ₂ O ₃	CaO	MgO	S	Cu	Fe	S	Cu	SiO ₂	FeO	Al ₂ O ₃	CaO	MgO	S
1932	55.3	17.0	4.3	4.6	0.1	0.8	14.9	78.8	0.6	19.4	2.3	42.9	10.9	11.8	23.4	2.9	0.01
1933	57.9	13.9	3.9	4.4	0.1	0.7	16.0	78.1	1.2	19.7	2.6	45.5	13.5	13.4	15.3	2.7	0.02
1934	56.7	12.7	5.8	3.9	0.2	0.6	17.2	71.8	5.8	21.0	1.9	45.3	18.5	13.3	12.5	2.7	0.15
1935	55.3	13.2	6.8	3.9	0.2	0.6	17.6	72.1	5.8	20.9	1.9	45.0	19.9	12.4	12.6	2.1	0.24
1936	54.7	12.8	7.7	3.6	0.3	0.7	18.3	67.0	8.7	21.7	1.2	40.4	20.3	11.4	15.0	1.7	0.25
1937	55.1	11.2	9.3	3.1	0.2	0.6	19.0	67.8	8.8	21.8	1.8	37.0	30.4	11.3	14.0	1.7	0.17
1938	53.6	11.5	10.4	3.3	0.2	0.5	19.7	68.2	8.5	22.1	2.0	38.4	32.5	11.9	9.6	1.6	0.18
1939	52.9	11.5	11.1	3.2	0.3	0.4	19.7	67.9	8.5	22.1	2.1	37.9	31.8	11.8	10.4	1.5	0.17
1940	51.8	13.0	10.8	3.5	0.3	0.5	19.3	67.4	8.8	22.1	1.5	38.0	29.9	11.7	12.5	1.6	0.22
1941	49.6	13.2	12.0	3.7	0.4	0.6	19.7	64.9	10.4	22.4	1.4	37.3	30.8	11.2	11.4	1.8	0.20
1942	48.8	12.2	13.7	3.4	0.4	0.5	20.8	63.5	11.5	22.7	1.4	36.2	34.3	10.1	11.8	1.6	0.28
1943	50.3	12.2	12.4	3.5	0.3	0.5	20.1	64.8	10.3	22.2	1.3	35.6	31.9	10.5	13.4	1.7	0.21
1944	51.1	14.1	9.7	4.1	0.3	0.6	18.2	66.7	8.8	21.7	1.2	36.9	25.1	11.2	17.8	2.2	0.17
1945	49.7	14.4	10.8	3.8	0.4	0.7	18.8	66.1	9.6	21.6	1.0	37.4	25.7	10.3	17.6	2.2	0.18
1946	51.5	14.8	8.9	4.0	0.3	0.7	18.0	68.0	8.0	21.4	1.1	38.3	22.3	10.9	20.3	2.1	0.14

To produce a blister containing less than the self-imposed maximum bismuth content it is frequently necessary to add duff coal to the charge. This ensures a reducing

if the lowering of grade is still insufficient to obtain satisfactory bismuth removal in the converters.

The comparatively high grade of the

matte produced coupled with the problem of bismuth elimination has meant that the operation of blowing the converters could not follow well-established

hopper is automatically stopped when this weight has been charged. The gross weight is obtained and printed. The drum is rotated 180° and dumps its contents into a

TABLE 2—*Reverberatory Furnace Tonnages*

Year Ending June 30	Concentrate, Tons	Reverts, Tons	Fluxes, Tons	Total Dry Solid Charge, Tons	Slag Produced, Tons	Matte Produced, Tons	Coal Burned, Tons	Fuel Ratio, Per Cent	Copper Produced, Tons	Tons Copper per Ton Coal Burned
1932	45,297	4,640	10,111	60,048	23,016	31,614	13,119	21.85	23,087	1.76
1933	75,890	11,155	8,474	95,519	24,198	61,967	17,199	18.01	42,170	2.45
1934	112,740	25,881	8,119	146,740	31,956	98,024	25,037	17.06	62,120	2.48
1935	150,070	30,742	12,443	193,855	45,882	129,795	33,095	17.10	82,212*	2.48
1936	158,920	33,194	14,149	206,263	49,500	141,032	34,482	16.72	86,997*	2.52
1937	178,043	43,358	14,204	235,605	55,311	164,439	40,427	17.16	95,438*	2.36
1938	165,444	53,732	8,295	227,471	50,214	152,252	39,970	17.57	87,165*	2.18
1939	151,820	42,233	9,183	203,236	48,538	139,035	37,498	18.45	78,850*	2.10
1940	166,590	26,284	13,424	206,298	57,687	144,773	35,615	17.26	84,219*	2.36
1941	166,363	22,835	13,605	202,803	59,202	137,557	34,631	17.08	79,912*	2.31
1942	171,630	24,548	14,220	210,398	63,993	147,436	39,463	18.76	81,583	2.07
1943	159,409	22,979	14,915	197,303	59,014	139,268	37,893	19.20	78,797*	2.08
1944	154,746	26,414	23,377	204,537	65,248	133,882	34,403	16.82	77,424*	2.25
1945	125,547	20,074	19,515	165,136	52,926	105,312	29,270	17.72	61,482	2.10
1946	118,326	17,261	22,876	158,463	53,804	95,538	27,418	17.30	59,908	2.18

* Includes a proportion of blister produced from the smelting of concentrate for the account of Mufulira Copper Mines, Ltd., Northern Rhodesia.

practice. This problem is fully dealt with under "Converting."

CONCENTRATE CONVEYING, WEIGHING AND STORAGE

Concentrate is delivered from the Oliver filters by belt conveyors to the three storage bins. Each of these has a capacity of 120 tons wet concentrate. From the bins the concentrate is discharged by belt feeders on to a 20-in. conveyor belt which delivers it to the weigh-hopper. This machine consists of a circular steel drum with dished ends. An opening is provided in the shell for charging and discharging concentrate. It is carried on a horizontal shaft which is rotated by an electric motor through reduction gears. The whole unit is carried on a frame set on knife edges. The capacity of the drum is 25 tons of wet concentrate. The operation of feeding conveyors, weigh-hopper and ticket printing mechanism are electrically interlocked and the weight cannot be printed unless the scalebeam is in balance. Any predetermined weight is set on the steelyard and the feed into the

receiving bin below. When the drum returns to the upright position, the tare weight is obtained and printed and charging of the next batch of concentrate commences. An automatic sampler and riffle chute are provided to sample the stream of concentrate as it discharges from the belt conveyor to the weigh-hopper.

The concentrate in the receiving bin is discharged by belt feeder on to a 20-in. belt conveyor which delivers it to the charge bins.

The charge bins consist of 18 steel compartments, in two parallel rows of 9 each. Each bin has a capacity of 2900 cu ft. One row of bins is reserved for concentrate and the other for fluxes and plant reverts. Material is charged to the bins by two 20-in. belt conveyors and distributed to each compartment by travelling trippers, one over each row. The contents of each bin is taken as a unit lot and the weight and analysis are known before it is charged to the furnace.

Each bin is equipped with a motor-driven apron feeder. This discharges on to

a 24-in. belt conveyor which runs down the centre line of the bins, delivering its contents to a 20-in. belt conveyor, 656 ft long, which carries the charge to the

contents on to a 30-in. belt conveyor. This discharges to a 24×15 -in. jaw crusher. The product of the crusher is then delivered in turn to a $5\frac{1}{2}$ -ft standard Symons cone



FIG 2—CHARGING WING TRIPPER ON TOP OF REVERBERATORY FURNACE.

smelter. Incorporated in this conveyor is a Dennison weightometer which records the weight of charge delivered to the furnace. Since the charge ingredients (concentrate, limerock, reverts and others) are fed on to the 24-in. belt simultaneously, they are well mixed after they have been discharged on to the four other belts which carry them to the furnace. All these conveyors and the apron feeder motors are operated by push button control on the feed floor of the furnace and are electrically interlocked.

The flux bins consist of six steel compartments, each of 3550 cu ft capacity. A standard gauge (3 ft 6 in.) railroad track runs over the top of the bins so that cars which deliver fluxes can be directly off-loaded into the bins. Plant reverts are delivered to these bins in bottom dump cars of 15 tons capacity. A travelling feeder runs under the bins and delivers their

crusher and a 42×16 -in. Allis-Chalmers rolls crusher which can operate either in open or closed circuit with 4×5 -ft Hummer vibrating screens. All units are served by the necessary feeders and conveyors. The crushed product is delivered to the charge bins by a 20-in. inclined belt conveyor.

REVERBERATORY SMELTING

Table 3 gives the dimensions of and information about the three reverberatory furnaces. The sidewalls are 24-in. thick and built of firebrick throughout, except in the settling zone where they are faced with 12 in. of magnesite brick from the furnace bottom to above the normal bath level.

All three furnaces have slag bottoms. During construction of the furnaces, the concrete foundations were lined with fire-

brick and protected with a layer of crushed slag. Blast furnace slag from Bwana Mkubwa was used for the bottom of No. 1 furnace. It was melted in a cupola and

poured into place through launders. Ordinary molten reverberatory slag from this furnace was used to pour the bottoms of Nos. 2 and 3 furnaces. Coal was burned in



FIG 3—TAPPING MATTE.

TABLE 3—Reverberatory Furnace Data

Furnace No.....	1	2	3
Year Built.....	1931	1934	1943
Length inside brickwork, ft...	120	120	95.5
Width inside brickwork, ft...	25	28	28
Uptake area, sq ft.....	150	125	140
Normal rating waste heat boiler, lb steam per hr....	40,000	61,500	80,000
Area of preheater elements, sq ft.....	10,500	14,500	21,870
Capacity of induced draft fan, cfm.....	92,000	92,000	142,000
Max. capacity per month, tons copper.....	5,500	8,000	8,500

Plant Losses

	PER CENT
Reverberatory slag.....	0.93
Reverberatory stack and unaccountable...	1.07
Converter stack and unaccountable.....	0.20
Total losses.....	2.20
Recovery.....	97.80
	100.00

both furnaces during the slag pouring operation and only when the correct level of molten slag had been transferred was the coal firing rate slowly reduced. This insured cooling of the bottom at a slow even rate to minimize cracking. In No. 3 furnace over 1300 tons of slag was used for the bottom.

When the Smelter went into operation in 1931, No. 1 furnace was equipped with the conventional sprung silica arch. The silica bricks were purchased in India. Campaigns were usually of three to four months duration.

The design of No. 2 furnace made pro-

vision for a suspended arch for the first sixty feet from the burner wall; the balance of the arch was to be of sprung silica brick. The brick used for the first campaign in

The acute shipping position after the commencement of the war all but cut off the supply of bricks from overseas. Two South African refractory manufacturers



FIG 4—CHARGING BLISTER COPPER TO HOLDING FURNACE. CASTING MACHINE STEAM HOOD AND STACK IN BACKGROUND.

the suspended section was an imported, unburned magnesite, 18-in. long. This roof lasted for ten months. However, the cost of these bricks per square foot of roof surface was 4.1 times as much as for a roof of high alumina firebrick, a type of refractory which at that time was attracting our attention. The conclusions then drawn were distinctly unfavorable to the basic roof.

During the succeeding five years the arches of both furnaces were changed to the suspended type. A combination of imported silica and high alumina firebrick was used. Campaigns were of five to seven months' duration and a great deal of hot-patching with high alumina brick was necessary during the last two months of each run.

quickly developed a brick comparable in all properties with the imported aluminous brick. At the same time we reviewed the position regarding the basic roof in view of the altered price of firebrick and the price of basic brick of South African manufacture. The picture had completely changed; the cost per square foot of roof surface for a 15-in. burned chrome-magnesite brick was now only 1.8 times as much as for a 20-in. aluminous firebrick. The cost, per pound, of the two types of brick is 2.55 pence for aluminous firebrick and 2.95 pence for chrome magnesite. We should have preferred to use a straight magnesite brick, but at the time the demands of the greatly expanded steel industry in the Union of South Africa for basic refractories



FIG 5—DISCHARGE END OF CASTING MACHINE AND FINNING CONVEYOR IN FOREGROUND.



FIG 6—POURING MOLTEN STEEL INTO COPPER BALL MOLDS.

rendered it impossible for the manufacturers to offer us anything but chrome-magnesite bricks.

A trial lot of 2,000 15- × 6- × 3-in. roof bricks was ordered and their performance in the combustion zone was so encouraging that we proceeded to equip No. 2 furnace roof with them for a distance of 50 ft from the burner wall. The arch of No. 3 reverberatory, which was under construction at the time, was similarly equipped. Beyond this basic section the arch was built with aluminous firebrick, of which we had a large stock on hand. When this reserve is exhausted we intend to install complete arches of basic brick.

The basic roof has more than come up to expectations, reducing reverberatory brick costs by more than 40 pct. Campaigns now run for twelve months, after which time the furnace is shut down for overhaul and inspection of the waste heat boiler. Advantage is taken during this shutdown to make any necessary repairs to the shoulders and flat section of the arch.

The only hot-patching necessary during a campaign is around the charge pipes. The charge thimbles last approximately two months. When installing a new one, two courses of brick surrounding it on three sides are replaced. For this hot-patching we use an unburned chrome-magnesite brick because of its superior spalling resistance when suddenly exposed to furnace temperatures.

The burner wall and uptake wall are built with basic brick. Water cooled copper blocks are incorporated in the uptake wall to prevent corrosion of the brick. The side-walls in the charging zone are built with standard fire brick to within 2 ft of the top. Above this they are of chrome magnesite blocks, 4 × 2 × 2 ft cast in position, when the furnace is shut down for repairs, from crushed and correctly sized brick cobbings.

The present method of arch suspension is shown in Fig 7. It is known locally as

the "Pin Type Suspension." Two bricks, each 15- × 6- × 3-in. are suspended together by a $\frac{3}{8}$ -in. diam mild steel pin which extends through the pinhole of each brick. This pin is supported by a $\frac{3}{8}$ -in. mild steel rod, 2-ft 3-in. long, bent over at both ends. The lower end fits into the rebate between the two bricks and supports the suspension pin. The upper end fits over a 2-in. pipe extending the width of the furnace. This pipe rests on the back-to-back channels which constitute the arch supporting steelwork.

The rebate between the bricks is filled with ground magnesite. This protects the suspension pin and lower part of the hook from corrosion by concentrate and dust. During the experimental period all bricks were "parted" with $\frac{1}{8}$ -in. steel wire mesh to insure complete bonding of the bricks. This resulted in abnormal growth of the arch. Experimental patches in which no parting material was used indicate that it is quite unnecessary. This is further corroborated by the assurance of the brick manufacturers that they are able to control the amount of magnesio-ferrite ($\text{MgO} \cdot \text{Fe}_2\text{O}_3$), the actual bonding cement, in their chrome-magnesite bricks.

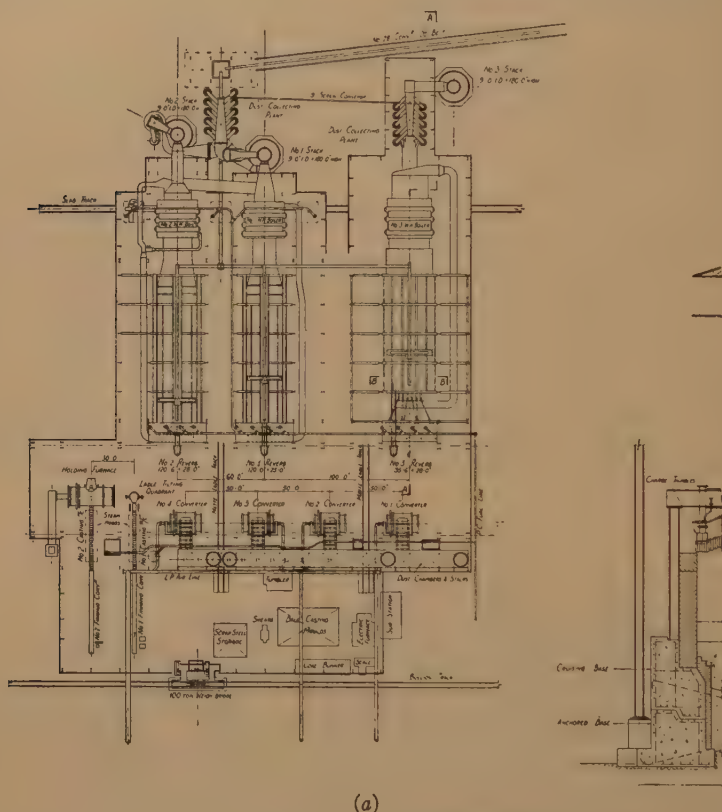
The type of charge thimble used is shown in Fig 7 (b). The box surrounding the 8-in. pipe is filled with correctly sized crushed magnesite grout and allowed to dry and set before use. Proprietary cements have been used instead of grout but have not given improved life.

The conventional method of steelwork construction for sprung arches was used with No. 1 furnace. The spacing between side buckstays in the front section of No. 2 furnace was increased because of the suspended arch. When No. 3 furnace was built, side buckstays were eliminated completely; the steelwork along the sides of this furnace acts solely as support for the furnace arch and charge floor. Nos. 1 and 2 furnaces are tied across the tops with 2-in. diameter tie-rods through the side buck-

stays. All burner and uptake walls are supported by vertical buckstays. These are tied in with the end buckstays carrying the longitudinal tie-rods, one on each side of the furnace.

by the wet charge. The charge takes up an angle of repose of 45° inside the furnace so that during a campaign there is little wear on the sidewalls.

Each furnace is equipped with a Stirling



(a)
FIG 7—PLAN OF PIN TYPE SUSPENSION.

The charge to the furnace is transported by a system of belt conveyors and distributed to either side of the furnace by a wing tripper which travels the full length of the furnace. Concrete lined hoppers on each side, adjacent to the sidewalls, receive the charge. From these the charge is fed to the furnace through 8-in. pipes spaced at 5-ft centres. Normally the furnace is charged three times each eight hour shift, though when operating at capacity it may be necessary to increase to four times. There is seldom any choking of the pipes

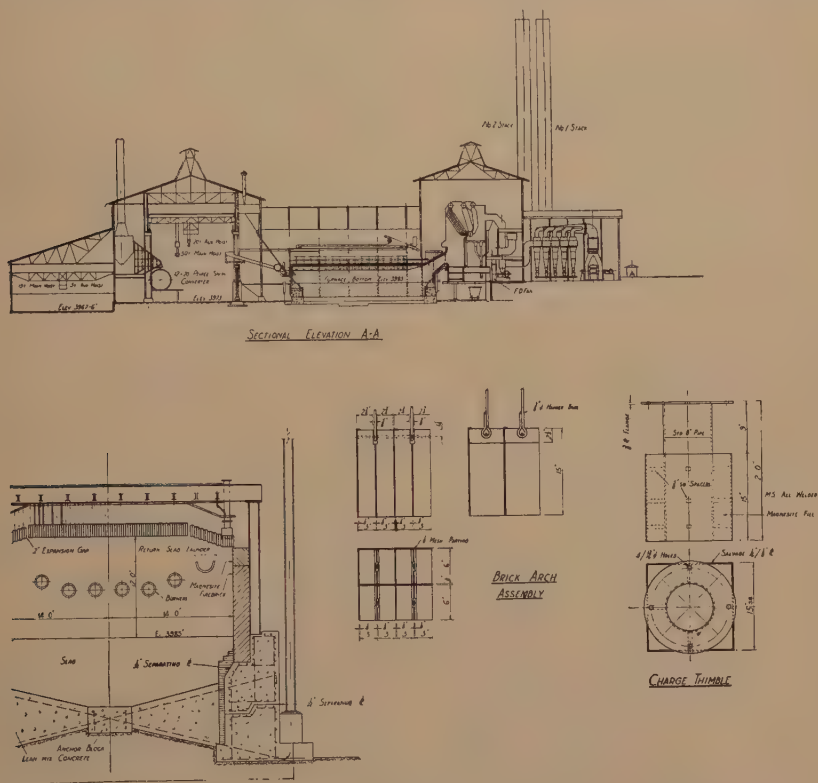
waste heat boiler, complete with Bailey walls, a USCO plate type air preheater, and Howden induced draught fan. Two Buell microelectors serve the three furnaces. Each furnace has a brick lined, steel stack, 9 ft id and 180 ft high. On Nos. 1 and 2 furnaces the induced draught fan is placed between the preheater and microelectors while on No. 3 furnace it is between the microelectors and stack. All furnaces are interconnected by steel flues provided with suitable dampers so that in an emergency, one or even two additional induced draught

fans may be used with the operating furnace.

Steam is generated in the waste heat boiler at a pressure of 275 psi ga and at a superheat temperature of 605°F. Preheated

moisture content of the solid charge is 7 to 8 pct there is a considerable amount of dusting in the furnace.

Pulverized coal is used as fuel. There is a central pulverizing plant which supplies



(b)
FIG 7—(Continued)

combustion air, at a temperature of 350 to 400°F and a pressure of 8 in. of water is furnished to the burners by a centrifugal forced draught fan. A small portion of this air is recirculated through the preheater to prevent condensation of moisture on the elements. The microlectors collect 87 to 90 pct of the copper in the dust entering them. This dust amounts to 3 to 4 pct of the total solid charge. The dust which falls to the bottom of the microlectors is fed by a system of screw conveyors to a surge bin situated directly over the main charging belt. Despite the fact that the

fuel to the power station and smelter. The raw coal, supplied from Wankie colliery in Southern Rhodesia, is received here, either in peanut size or duff. It is dried in Ruggles-Coles driers and pulverized in three 8-ft X 60-in. air swept Hardinge Ball mills coupled with super-fine classifiers. The classifier discharge is batch weighed and then transported by Fuller-Kinyon pumps to the storage bunkers at the smelter or power station. The coal is pulverized to 70-80 pct minus 200 mesh. A representative sample assays:

	Pct
C.....	78
H.....	4.5
S.....	1.3
O.....	4.5
N.....	1.6
H ₂ O.....	1.1
Ash.....	10.1
Volatile.....	27.5
Btu per lb.....	13,600

The coal is pumped to steel bunkers, four to each reverberatory furnace, situated directly above the firing end. Each bunker has a capacity of 18 tons and is equipped with a Bailey feeder driven by an electric motor through variable speed reduction gears. No primary air is used for combustion. The coal falls by gravity from the feeder through a three inch line into the burner tip; there it mixes with the pre-heated combustion air and is blown into the furnace. Excellent mixing of coal and air is achieved in this manner. Four or six circular burner tips, 16-in. diam spaced at 3-ft centres, are installed on each furnace. The center line of the burner tips is 7 ft below the bottom of the arch and 5 ft above the slag bottom. A short flame is generally used, though when the matte grade increases unduly, it is found advisable to increase the length of the flame so as to minimize the oxidation of iron sulphides in the charge. Orsat gas analysis usually shows 1.0 to 1.2 pct oxygen in the gases 80 ft from the burners. The furnace draught is kept at 0.025 in. of water. The draught is controlled through dampers on the inlet to the induced draught fan.

The hot secondary air is conducted to the burners through 4-ft diam insulated ducts. An orifice plate installed in these ducts is connected to an inclined draught gauge which indicates the flow of air to the burners. This permits careful control of the amount of combustion air. Distribution of air to each burner is controlled by butterfly valves placed in each branch line. The volume of air supplied by the forced draught fan can also be controlled by movable vanes at the inlet of the fan.

Matte is tapped through either of two

tapholes, situated 70 and 75 ft from the burner walls. The tapping block consists of a burned chrome brick cast in a low-blister copper block which is wedged into a steel breast plate. Two 2½-in. diam holes, at 9-in. centres are provided in the brick when manufactured, thus furnishing two tapholes in the same block. The taphole is opened with an oxygen lance and closed with a clay dolly. A tapping bar is inserted in the taphole after closing but matte seldom "follows" the bar when it is removed because of the high melting point of the matte. The temperature of matte as it runs from the furnace is 2010°F.

One matte tunnel serves both Nos. 1 and 2 furnaces. No. 3 furnace is provided with a matte tunnel on each side. Molten matte is run into cast steel ladles, of 150 cu ft capacity. They are carried on bogeys which are operated by an electrically driven wire rope haulage on tracks which extend into the converter aisle. Beyond the matte launder is space for three ladles so it is not necessary to shut off the taphole during tapping.

The skimming bays are situated in the sidewalls of all three furnaces, 110 ft from the burner wall on Nos. 1 and 2 furnaces and 85 ft on No. 3 furnace. The sills of the skimming bays are 24 in. above the level of the lower taphole. Slag is conveyed by launder into hematite iron pots of 200 cu ft capacity, in a tunnel running at right angles to the centre line of the furnaces and just beyond the uptake walls. The slag pots are carried on bogeys which incorporate an electric tipping mechanism. The train of three pots is hauled to the slag dump by a 20-ton Jeffrey trolley loco. Slag is also skimmed into ladles in the matte tunnel when it is required as converter flux. The temperature of the slag is 2200°F when skimmed from the furnace. The molten bath in the furnace is usually 20 to 24 in. of matte and 6 to 9 in. of slag.

Molten converter slag is returned to the furnaces through cast iron launders, dis-

charging through the centre of the firing wall on Nos. 1 and 2 furnaces and adjacent to the west sidewall on No. 3 furnace. This latter position has not caused any inconvenience in operation.

Beneath each waste heat boiler is an ash hopper with cleaning doors slightly above floor level. All dust and cleanings that fall from the boiler tubes are rabbled out, wetted down and transported to the main charging belt for addition to the furnace charge. An auxiliary coal burner is situated in each of the ash hopper side walls so that any accretions which form on the uptake or Bailey walls of the boiler can be smelted down while the furnace is operating.

Difficulty has been experienced from time to time with "blowbacks" in the furnaces. This is caused by sliding of the charge piles when undercut by the bath of molten matte. The moisture in the concentrate is responsible for the almost explosive nature of the blowback. Experience has shown that when a particular pile has slid into the center of the furnace the only way to prevent recurrence is to smelt down the pile completely and then to build it up again slowly, generally over a period of two days. In this manner all moisture is evaporated from each section of the pile before the next addition is made.

During a normal one year campaign the hearth of an operating furnace builds up to a depth of as much as three feet with magnetite. This is introduced with the converter slag, and all attempts to limit its settling on the bottom of the furnace have been without success. Towards the end of a furnace campaign tonnage of charge treated per day decreases, the fuel ratio increases several points and because of the decrease in the depth of molten bath the copper values in the slag increase. After the furnace has shut down and cooled off this build-up is drilled and blasted out. The effect of blasting on concrete foundations is not good, but until the grade of matte decreases to a point where the amount

of magnetite formed in the converters can be controlled, there is no economic alternative.

Assays of concentrate, matte and slag are given in Table 1. Furnace tonnages and other data since the commencement of operations are given in Table 2. The fuel ratios obtained are better than would be expected with a charge containing 7 to 8 pct moisture. This can be explained by the high proportion of matte forming elements present in the charge.

CONVERTING

Converting equipment comprises four basic lined Peirce-Smith converters, 12 ft in diam and 20 ft long, inside the shell. Each is equipped with 30 1½-in. tuyeres spaced at 6-in. centers. They are lined with 12-in. chrome-magnesite brick backed with a 4½-in. layer of fire brick. The thickness of the magnesite brick used along the tuyere line is 18 in.

The converters are rotated by 35 hp Holman air motors through reduction gears and operated by compressed air at a pressure of 90 psi. An air receiver at the smelter equipped with a non-return valve, has ample capacity to turn a converter out of the stack in case of a failure in the compressed air supply.

The mouths of the converters are 5-ft square and are lined with cast steel frames. Gases from the converters discharge through a cast iron hood into the common flue and dust chamber behind the converters. From this the gases are discharged to atmosphere through four 5-ft diam stacks the tops of which are 66 ft above the roof of the dust chamber. About 90 tons of flue dust are collected each month in this flue and in the converter hoods. The dust is returned to the circuit through the reverberatory furnaces.

Converter air is supplied by three low pressure blowers, situated in the power station. The air is conveyed to the smelter through 30-in. diam pipe lines. One blower

is a Bellis and Morcom four crank single stage vertical compressor, driven by a 950 hp electric-motor, and has a rated capacity of 15,000 cfm free air at 15 lb psi pressure. The other two blowers are Brown-Boveri single cylinder, four stage steam turbo-blowers, connected to single cylinder combined type turbines which are driven by steam at a pressure of 250 psi and a temperature of 650°F. The capacity of each of these blowers is identical to the electrically driven blower.

The converters are heated with pulverized coal which is blown through a burner port situated in one end wall. Each

auxiliary travels on the lower inside flanges of these girders. The two hoisting motors are electrically synchronised as a precautionary measure when lifting ladles of molten material, and are provided with overwind devices of local design.

The cast steel ladles used are provided with detachable rings which carry the two lifting lugs. These rings are periodically removed and shipped to the Union of South Africa for annealing. When a ladle bottom cracks or shows abnormal wear, it is cut out and a circular cast steel disc, 4-in. thick, is welded in its place. In this manner the life of a ladle is extended to

TABLE 4—*Miscellaneous Assays*
By Percentage

	Cu	SiO ₂	FeO	CaO	Al ₂ O ₃	MgO	S	Fe
Limerock.....		2.20	0.35	52.5	0.60	0.85		
Converter slag.....	7.75	25.4	41.0	11.1	7.00	1.20	1.45	
Reverts.....	16.25	18.9	26.2	7.05	5.65	1.35	7.60	
Conv. flue dust.....	67.40						11.2	1.90
Silica flux.....		90.5						

converter is provided with a coal bunker of 9 ton capacity, to which is attached a variable speed Bailey feeder. The coal is blown into the converter from the feeder discharge with air provided by a Sturtevant primary air fan; no secondary air is used. Before the commencement of a blow, the burner port is closed off with clay. This is removed at the end of the blow when the coal fire is restarted. Due to the high grade of matte and the problem of bismuth removal it is essential to have coal burning equipment on the converters to bring the shells up to full heat after a shutdown and to keep them hot between blows.

The converter aisle is serviced by two Thomas Broadbent dc overhead cranes of 57-ft 6-in span. The main and auxiliary bogeys operate independently of each other both in hoisting and traversing. The main bogey, with a lifting capacity of 50 tons, travels on rails attached to the top surfaces of the crane girders and the 20 tons

over six years. The bottoms of ladles are protected with a pad of reverberatory slag when tapping matte, and the whole of the inside of a ladle is protected with a shell of converter slag when it is used for handling molten copper. The ladles are cleaned of skulls by suspending them from the crane and bumping against a large copper block situated in the converter aisle. The production of ladle skulls is not unusually high considering the grade of matte treated.

Ladles are moved in front of converters on bogeys which travel on standard gauge railroad tracks on ground level extending under the shells. The tracks have a slight downward grade and the bogeys are moved by a wire rope attached to the auxiliary hoist of the crane through a sheave anchored in the floor of the converter aisle. This provision is necessary as a converter must be emptied completely at the end of each blow, or the bismuth content of the following charge will be abnormally high

All converter aisle cleanings, sweepings and ladle skulls are handled in boats of suitable size and dumped on to a grizzly situated at the east end of the aisle. From the grizzly they fall into bottom dump cars which are hauled to the flux bins by a Vulcan diesel-electric locomotive.

Converting operations differ in the following respects from established practice at other smelters of comparable size; 1. Smaller converters used. 2. Exceptionally high grade of matte treated. 3. The necessity for running a higher temperature than is considered good practice so as to produce a blister copper sufficiently low in bismuth to permit of one straight fire refining operation. 4. Method of fluxing. 5. No attempt is made to splash on a protective lining of magnetite.

The 20 X 12-ft converters were decided upon in the original design with the object of conserving as much heat as possible when treating a matte containing 78-79 pct copper. With the present grade of matte this point is no longer of such importance. This size converter, however, permits more flexibility because of its smaller capacity.

Bismuth removal in converting increases with rise in temperature of the bath, especially during fluxing when over 50 pct of the total bismuth removal is achieved. The temperature rises during this period to over 2410°F. Scrap copper cannot be added after the final skim; apart from the fact that this would chill the bath, it has been found that bismuth is extremely soluble in metallic copper, and once dissolved it cannot be removed thereafter by blowing. Copper scrap is added 20-30 min before the end of the blow; after this stage no further bismuth removal takes place. No plant reverts, including matte ladle skulls, can be smelted in the converters.

During the initial two years of plant operation no converter flux was necessary but when the matte grade fell below 72 pct copper, molten reverberatory slag was introduced as a flux. Because of the relatively

high melting point of the matte and the lack of iron for the production of heat, the use of silica for this purpose was ruled out. In addition silica flux would chill off the charge causing an increase in the bismuth content of the final blister.

The use of reverberatory slag alone as a flux possesses several disadvantages: 1. The small amount of available silica in the slag. Because of the daily variation in slag analysis it is difficult to standardise a system of fluxing. 2. Used at the rate of 12 tons of slag per 60 ton charge of matte (three ladles) the slag increases the burden on the tuyeres. This entails harder and almost continuous punching and reduces the life of the tuyere line. 3. Slag cannot be added until at least 25 min after the commencement of the blow or the whole charge would foam. This restriction favors the formation of excess magnetite which is returned to the furnace and builds up the hearths. It also leads to the formation of sows inside the converter.

In 1944 partial silica fluxing was introduced in an effort to alleviate the unpleasant features attendant upon the use of molten slag. 1½ tons of crushed quartzite (90 pct SiO₂) is charged into the converter ten minutes before adding the first ladle of matte. By the time the third and final ladle has been charged the flux has been well heated and the blow commences. Blowing continues until all the iron has been oxidized, a matter of 35 to 45 min. 7½ tons of molten slag are charged and blowing is continued for a further 3 to 5 min. Slag is skimmed in the usual manner, 12 to 15 tons being taken off. The copper blow then commences.

The replacement of all slag by silica has been tried but has not proved altogether successful. The bismuth content of the blister exceeded the permissible limits because the temperature attained during the blow was too low. The quantity of silica charged was reduced to an amount which was calculated to produce a viscous slag,

and interesting results were obtained. Slags of low silica content (13 pct SiO_2 , 72 pct FeO) were quite fluid and of low copper content, but they contained up to 50 pct magnetite.

On several occasions an attempt has been made to blow a magnetite lining on to the brickwork. We adopted the normal procedure followed when treating a matte containing 45 pct copper. None of these blows has been a success for, while a lining was blown on, it was too thin and uneven and was washed off by the succeeding blow. Taking account of the low iron content of the matte and the high temperature reached during the fluxing period of the blow it is not considered feasible to blow on a durable lining when the matte grade is above 62 pct copper.

The life of a converter tuyere line averages 150 blows; on occasions as many as 225 blows have been obtained. The wear on the lining is generally restricted to the tuyere line and 2 ft above it. Brick consumption varies from 2.75 to 3.0 lbs per ton of copper produced.

Converter Data

Average charge, tons matte.....	53.5
Scrap copper remelted, tons per charge.....	2.9
Blowing time per charge, min.....	150
Minutes per ton matte blown.....	2.8
Minutes per ton blister produced.....	4.5
Blister produced per charge, tons.....	33.5
Fuel consumed for heating, tons per day.....	7.1
Fuel, pct matte treated.....	2.6

CASTING

The casting equipment consists of two straight line casting machines, each carrying 50 molds. One is served by a 13 × 30-ft rotary holding furnace and the other by a ladle tilting quadrant. The machines extend from the converter aisle into the casting aisle. The ladle tilting machine is only used for special casts or on the infrequent occasions when the holding furnace is shut down for repairs. Both machines are operated from a central control cabin.

The holding furnace is lined with 12 in. of basic brick backed by 4½ in. of insulating brick. It is rotated through reduction

gears by a 50 hp electric motor. It is fired with pulverized coal through one end wall. The products of combustion discharge through a goose-neck flue from the end opposite the coal burner, to a horizontal brick flue and thence to a brick stack 60 ft high. A 2-ft square skimming door is located in the shell at each end, the centre of the door being 3 ft from the end walls. Slag is skimmed once per day into boats carried on bogeys running on tracks directly under these doors. The slag is dumped on the grizzly, broken up and returned to the plant with the furnace charge.

The charge opening of the furnace, 3 × 3 ft 3 in. is closed with a copper door which is lined with basic cement. The levers attached to the door are secured to the furnace foundations with chains. On tilting the furnace back to receive a charge of copper from the converter aisle crane, the door is automatically lifted. Copper is cast from the furnace through a 3 × 6-in. taphole into a brick-lined spoon set directly over the line of molds on the casting machine. A normal casting rate is 30 sec per 350 lb cake. This is equivalent to 21 tons per hour.

In their progress to the discharge end of the machine the copper cakes are cooled by water sprays under an asbestos-cement lined hood. The steam generated is carried away through a wood stack. As the molds turn over the head pulleys of the casting machine, the cakes are loosened with bars and fall on to a chute which discharges them to a finning conveyor. On this slow moving conveyor they are trimmed before being loaded by barrows into railroad cars for shipment. The cars are moved by an endless wire rope haulage on to a 100 ton weighbridge. On this scale the cars are weighed before and after loading to obtain the weight of blister shipped. All fins, cleanings and rejected cakes are returned to the converters for remelting.

The casting machine molds are cast from low-blown blister copper in demountable

cast iron master molds, from a ladle suspended from the crane in the converter aisle. A cast iron pouring plate is embedded in the bottom of each mold to receive the stream of copper from the pouring spoon during casting. The Roan Antelope brand mark, "RA," is also embedded in the bottom of each mold. When a mold is worn out it is broken up to recover the cast iron pouring plate and the copper is remelted in the converters.

Each railroad car shipped is taken as a unit lot. During casting, spoon samples are taken at frequent intervals as the copper flows from the holding furnace and are "shot" by pouring into water. The whole sample is carefully screened to remove oversize before being sent to the assay office.

The casting aisle and adjoining steel foundry are served by an electric overhead travelling crane. The main hoist of this crane has a capacity of 15 tons and the auxiliary a capacity of 5 tons.

Casting Data

Average weight per cake, lb.....	355
Coal consumed for heating, tons per day....	4.7
Coal, per cent of copper cast.....	2.7
Molds consumed, pct of copper cast.....	1.5
Average analysis of blister, pct Cu.....	99.4

PERSONNEL

The European operating personnel of the smelter is composed of 24 men. Nine of these are on the salaried staff (superintendent's department, general foreman, shift foremen, fitter foreman), three are bricklayers and two are repair fitters. The reverberatory furnace, overhead crane and converters each require one European per shift. The concentrate weighing and flux crushing is handled by one man on day shift. Operation of the waste heat boilers is under the control of the power station.

The African personnel varies between 240 and 250. They are divided among the various sections of the plant as follows:

Reverb. furnaces and charge conveying.....	63
Converters.....	69
Casting, loading and weighing.....	45
Concentrate handling and flux crushing.....	17
Bricklayer helpers.....	13
Fitter helpers.....	10
Plant clean-up and maintenance.....	19
Superintendent's department.....	4

Total..... 240

Smelter Costs By Elements

ITEM	COST SHILLINGS PER SHORT TON BLISTER PRODUCED
European labor.....	7.46
African labor.....	5.34
Supplies.....	6.11
Fluxes.....	3.59
Duff coal.....	1.60
Reverb. bricks.....	1.79
Conv. bricks.....	1.51
Shops.....	3.62
Power plant repair gang.....	0.14
General outside gang.....	0.29
Transport.....	0.58
Reverb. coal.....	12.80
Converter coal.....	1.16
Casting coal.....	0.75
Electric power.....	0.83
High pressure air.....	0.97
Converter air.....	2.50
Water.....	0.05
Motor cars.....	0.07
Assaying.....	0.85
Sundries.....	0.56
Waste heat credit.....	8.46
Total.....	44.11

Smelter Costs by Processes

PROCESS	COST, IN POUNDS PER SHORT TON BLISTER PRODUCED
Concentrate preparation.....	0.017
Charge preparation.....	0.033
Reverberatory smelting.....	0.977
Converting.....	0.694
Casting.....	0.163
Sampling and assaying.....	0.051
Overhead.....	0.270
Total.....	2.205

Power Consumption

ITEM	KW-HR PER TON OF BLISTER
Concentrate conveying and weighing....	1.33
Flux preparation.....	1.11
Charge preparation.....	1.46
Reverberatory conveying.....	1.88
Reverberatory coal feeders and fans....	5.66
Reverberatory draught fans.....	11.33
Slag disposal.....	0.53
Mud mill.....	0.36
Converter coal feeders and matte haulage	1.67
Overhead cranes.....	2.50
Casting.....	0.42
Holding furnace.....	0.21
Lighting.....	2.63
High pressure air (electric).....	15.75
Converter air (electric).....	4.78
TOTAL ELECTRIC.....	51.62
STEAM (kw-hr equivalent).....	18.60
High pressure air.....	82.02
Converter air.....	
TOTAL STEAM.....	100.62
GRAND TOTAL.....	152.24

STEEL FOUNDRY

Situated at the east end of the casting aisle is the steel foundry, where steel grinding balls and ball mill feed end liners are produced. This section of the plant is operated by the smelter.

The steel melting equipment consists of one 2-ton Heroult, 3 phase, electric furnace, with hydraulic electrode control. Water pressure is supplied by an electrically driven high speed centrifugal pump. The water supply to the electrode lifting rams is controlled by current relays which in turn operate relay control valves.

Power to the furnace is supplied by a 900 kva stepdown transformer, situated in a substation adjacent to the furnace. Current from the power station is supplied at 3300 volts. The secondary tapping from the transformer is 126 volts. Alternative tappings of 150 and 86 volts are also provided but are seldom used. The normal operating load on the furnace is 4000 amp. All controls, meters and switches are located on a central panel.

Three 7-in. diam graphite electrodes carry the current to the bath of the furnace. The electrode arms carrying the electrodes serve as the electrical conductors, and water cooling pipes are embedded in the clamps.

The roof, sidewalls and bottom are built of silica brick. A roof usually lasts for 250 heats and the sidewalls 150 heats. The bottom is fettled with crushed silica at the end of each heat and consequently is never replaced. The 1-ton ladles used for transporting the molten steel are lined with firebrick, and are heated on coke-fired forges between casts.

The 4-in. diam grinding balls are cast vertically in two piece low-blister copper molds. These molds are cast in the converter aisle on a cast iron core surrounded by a machined copper mold cap. Twenty-four complete molds, twelve to a row, are supported by and slide on railroad rails

welded to 10-in. I beams which constitute the mold-supporting racks. After pouring molten steel into the molds it is allowed to cool for five minutes before the molds are parted to allow the cluster of balls to fall to the ground. The clusters are broken up by hand after which the balls are cleaned in an electrically driven tumbler. A small proportion of the product requires further hand trimming. Fifteen balls are cast in each mold. Feed end liners are cast in open top copper molds with 1½-in. bolts cast in the liner. They are slowly cooled in sand after removal from the molds.

The charge to the furnace consists of discarded steel railroad sleepers, second hand rails, miscellaneous plant scrap and gates, risers and fins from the foundry. All scrap steel is cut to size on shears or by oxy-acetylene torch. No attempt is made to refine the steel; the operation may be regarded as one of straight melting. To increase the capacity of the furnace and save power by lowering the melting point of the steel a large proportion of fine coke (140 lb per 2-ton charge) is used. The carbon content of the steel is consequently high, 1.6 to 1.8 pct. A further benefit derived from the high carbon content is the relative brittleness of the ball clusters which permits ease in breaking them apart.

At intervals the furnace charge is made up of scrap cast iron for the production of pouring plates for blister copper molds. These are also cast in low-blister copper, open top molds. During one of these runs five hundred are cast, which constitutes a three to four months' supply.

Tonnage and efficiency figures for a typical operating year are set out in the table below.

Tons new scrap steel charged.....	2124
Tons foundry reverts remelted.....	586
Total tons steel melted.....	2710
Tons castings produced.....	1955
Recovery, per cent.....	92.05
Power consumption, kwh per ton melted...	600
Power consumption, kwh per ton castings..	831
Electrode consumption, lb per ton steel melted.....	7.5

One European and twelve Africans per shift are required to operate the furnace and foundry. The Africans are distributed as follows:

Furnace operation.....	2
Crane driver.....	1
Ladle.....	1
Mould setting.....	2
General laborers.....	6

In addition 6 Africans are employed on day shift trimming and cleaning balls, and

one European and an African helper are employed on scrap cutting.

This article brings up to date the smelting operations at Roan Antelope described by the late C. R. Wraith, original Smelter Superintendent at Roan, for the New York meeting of February 1934, and reported in *Transactions AIME*, **106** (1933).

Evidence of Formation of Copper Ferrite from Reaction between Cuprous Oxide and Copper Reverberatory Slags

BY PEI-YUNG HUANG,* STUDENT ASSOCIATE, AND CARLE R. HAYWARD,† MEMBER AIME
(New York Meeting, March 1947)

IN order to understand more fully the actual state of copper lost in copper reverberatory slags, a systematic study on the various reactions between certain metallurgically important copper compounds and synthetic copper reverberatory slags was undertaken by the authors in the Massachusetts Institute of Technology from 1942 to 1945.¹ This paper, being only a part of the work completed, is published first because it furnishes the first experimental evidence of the formation of copper ferrite from reactions between cuprous oxide and copper reverberatory slags.

CHOICE OF SLAG COMPOSITION

The choice of the composition of the synthetic reverberatory slags to be used was much deliberated. Commercial copper reverberatory slags, neglecting minor constituents, average:^{2,3} 45 to 47 pct FeO; 38 to 42 pct SiO₂; 5 to 6 pct CaO; 5 to 6 pct Al₂O₃. Since the ternary system CaO-FeO-SiO₂ has been much more thoroughly studied⁴

and is much simpler than the quaternary system CaO-FeO-SiO₂-Al₂O₃, it was decided to use calcium oxide only instead of calcium oxide and alumina in the synthesis of the slags. Fortunately the composition of the average copper reverberatory slag with calcium oxide substituted for alumina lies in the region of the phase diagram clarified by the investigators.

A survey of the phase diagram (Fig 1) suggested two compositions: (1) the composition near the invariant point *S*, which is made up of 46 pct ferrous oxide, 37 pct silica and 17 pct calcium oxide; (2) the composition near the invariant point *K* with 45.5 pct ferrous oxide, 43 pct silica and 11.5 pct calcium oxide. Composition *S* has the advantage that the percentages of ferrous oxide and of silica almost exactly coincide with those of the average reverberatory slags, and that of the lowest melting point ($1093^{\circ} \pm 3^{\circ}\text{C}$) in the whole ternary system. The calcium oxide content, however, obviously is high. Since we have already substituted calcium oxide for alumina, and since calcium oxide is more basic than alumina, the resulting slag is decidedly too basic. Composition *K* has a slightly higher melting point ($1105^{\circ} \pm 3^{\circ}\text{C}$) and a higher silica content, but this is preferred because the slag is saturated with respect to tridymite and thus should not corrode siliceous refractories. Besides, it is less basic than composition *S*. The final slag composition, therefore, was chosen to

This paper is based upon one part of a thesis submitted by Pei-Yung Huang in partial fulfillment of the requirements for the degree of Doctor of Science at the Massachusetts Institute of Technology. Manuscript received at the office of the Institute Aug. 15, 1946. Issued as TP 2140 in METALS TECHNOLOGY, April 1947.

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¹ References are at the end of the paper.

be 47.5 pct ferrous oxide, 42 pct silica and 10.5 pct calcium oxide.

The ferrous oxide in the slag was supplied by a calculated amount of pure

to 1200°C in a rotating induction furnace. The rotating induction furnace was used by the authors primarily for estimating the solubilities of various copper mattes

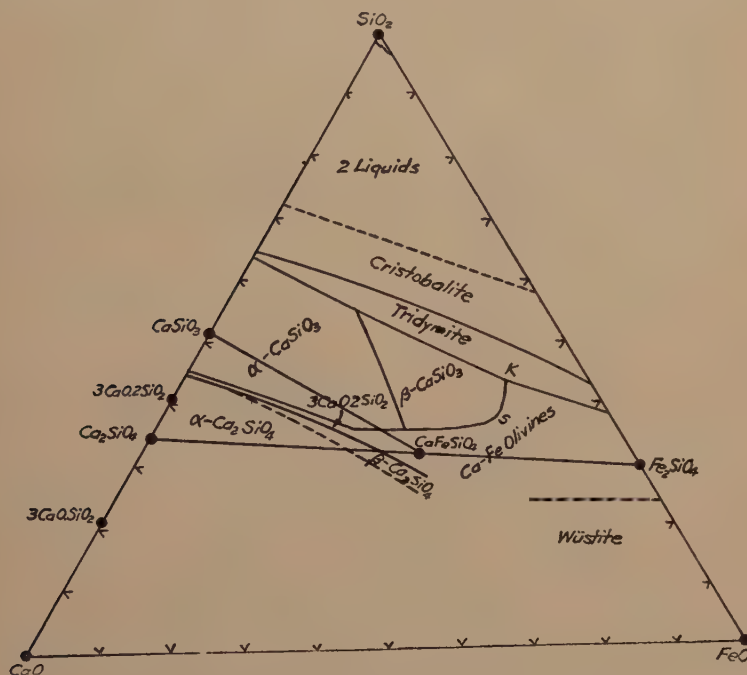


FIG 1—PHASE DIAGRAM.

ferrous oxalate ($\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$). Fe_3O_4 and Fe_2O_3 mixed with fine iron powder, calculated to yield the desired amount of ferrous oxide, were also tried, but they were not as satisfactory because the slags formed contained a very high percentage of ferric iron (more than 10 pct Fe_2O_3) and had a very high melting point, unless they were heated for a long time in a reducing atmosphere. Slags freshly prepared from oxalate are very fluid and analyzed generally less than one per cent Fe_2O_3 .

EXPERIMENTAL DETAILS AND APPARATUS

The synthetic slags were made by mixing together thoroughly weighed amounts of powdered silica, calcium oxide, and ferrous oxalate and heating in fire-clay crucibles

in synthetic slags,¹ but was found to be very convenient for studying the reactions between cuprous oxide and synthetic reverberatory slags. The construction of the furnace (Fig 2) is essentially the same as that of the one used by C. R. Taylor and J. Chipman⁵ in the study of equilibria of liquid iron and slags, only the construction of the crucible part being different. Fig 3 gives the detailed construction of the crucible.

Fire-clay crucibles were found to be satisfactory. The heating element was a piece of graphite machined out of a section of graphite electrode to contain the fire-clay crucible. It was found by experience that the top part of the graphite usually was oxidized and became porous after a number of runs, in spite of the

care taken to cover it with powdered graphite to prevent excessive oxidation of the graphite piece. Therefore a replaceable graphite part *B'*, in the form of a

A refractory tube *H*, made of zirconia, was outside the two crucibles. Coarse, electrically fused magnesia *E* was packed loosely around crucible *C* for insulation,

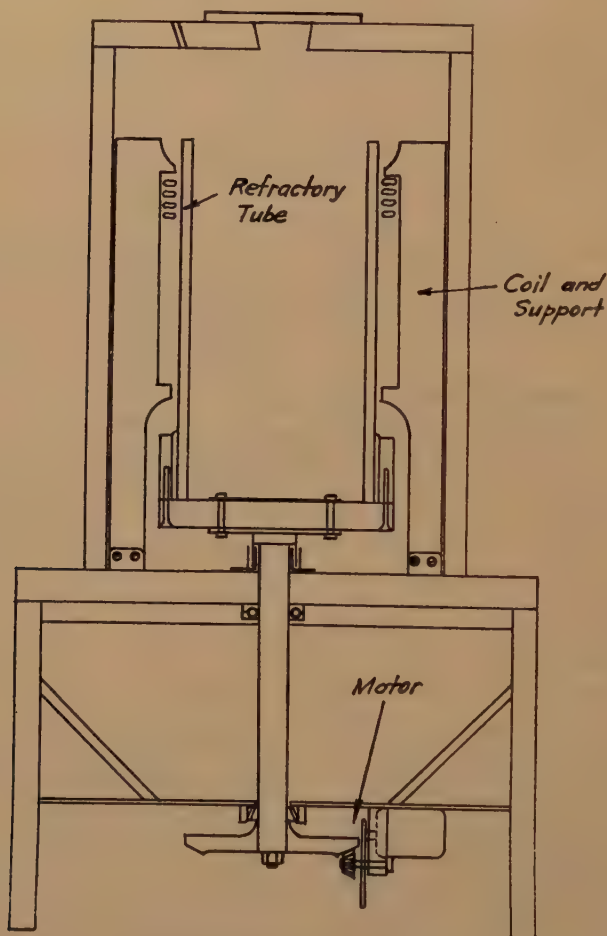


FIG 2—CONSTRUCTION OF FURNACE.

cylindrical ring, was used, which could be replaced by a new ring whenever necessary. *B'* was covered with graphite powder *D*, to prevent excessive oxidation.

Another crucible, *C*, was used as a container for the graphite heating element; it was found to be very convenient for insulation and for occasional removal of the graphite element for repairing and replacement.

and a ring of asbestos board separated the magnesia from a layer of powdered graphite and carbon black *G* placed next to the zirconia tube *H*. The *G* layer was for insulation and also to supply room for expansion, which often was considerable and might crack the outside tube.

An asbestos board *J* covered the magnesia grains to prevent the loosely packed

grains from spilling during the rotation of the crucible.

The induction coil was made of a hollow water-cooled copper tubing.

Calculated amounts of pure, finely powdered silica, calcium oxide, and ferrous oxalate were thoroughly mixed, and then heated to 1200°C in the rotating furnace. When a fluid slag was formed, a weighed portion of cuprous oxide was added all at once. The mixture was thoroughly agitated by rotation of the crucible, kept at 1200°C for about 20 min, and finally cooled in air.

Slags with initial cuprous oxide concentration of 5.0 pct, 9.5 pct, 17.4 pct, 24.0 pct, and 34.5 pct, respectively, were prepared. They all formed fluid slags at 1200°C, but the fire-clay crucibles showed very little sign of being attacked, presumably because of the briefness of contact. The solidified slags were all hard and gray. Very pronounced crystalline structure could be seen in the slags with very high initial cuprous oxide contents. The various slags finally were sampled for X-ray investigation, microscopic examination, and chemical analysis.

X-RAY INVESTIGATIONS

At the time of the experiments, which was before the publication of the First Supplementary Set of Cards of Alphabetical Index of X-Ray Diffraction Patterns by the American Society for Testing Materials, the complete d -values for the X-ray diffraction patterns of copper ferrites were unknown to us, therefore it was necessary for us to determine them. Cupric ferrite, $\text{CuO} \cdot \text{Fe}_2\text{O}_3$, was prepared by the methods of Wartmann and Thompson,⁶ by dissolving calculated amounts of copper and iron together in nitric acid, precipitating the mixed hydrated oxides with dilute sodium hydroxide solution, heating the washed precipitates to 1000°C for about an hour, and finally quenching the product in water. The product was

grayish white and strongly ferromagnetic. Analysis showed it to be pure $\text{CuO} \cdot \text{Fe}_2\text{O}_3$. The X-ray diffraction pattern of the sample is shown in Fig 4, together with

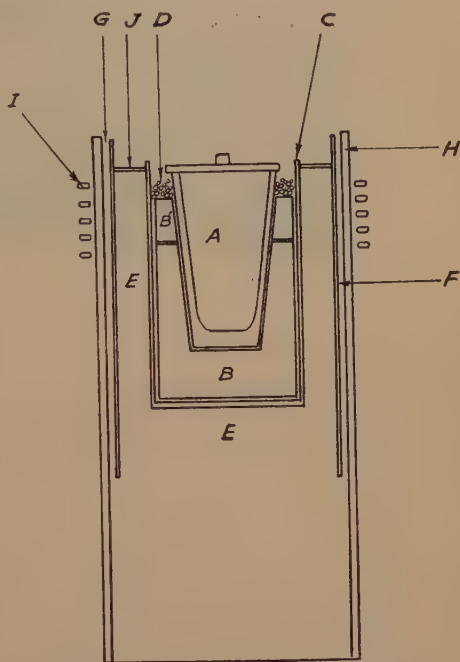


FIG 3—CONSTRUCTION OF CRUCIBLE.

- A. Crucible.
- B. Heating element.
- B'. Graphite ring.
- C. Crucible container for heating element.
- D. Graphite powder.
- E. Coarse, electrically fused magnesia.
- F. Ring of asbestos board.
- G. Powdered graphite and carbon black.
- H. Refractory tube of zirconia.
- I. Induction coil.
- J. Asbestos board.

an X-ray diffraction picture of magnetite: They are very much alike.

Cuprous ferrite, $\text{Cu}_2\text{O} \cdot \text{Fe}_2\text{O}_3$, was prepared by heating an excess of cuprous oxide over the calculated amount to form $\text{Cu}_2\text{O} \cdot \text{Fe}_2\text{O}_3$ with Fe_2O_3 to $1120^\circ \pm 20^\circ\text{C}$ for about half an hour, and quenched from that temperature by water spray. The mass was then powdered in an agate mortar, boiled with potassium cyanide solution to remove the cuprous oxide

in excess, washed, and then dried. It is dark gray in color, very hard and brittle. It contained 39.8 pct copper and 55.4 pct Fe_2O_3 . (Pure $\text{Cu}_2\text{O}\cdot\text{Fe}_2\text{O}_3$ should contain

each other easily, depending on the temperature used, $\text{Cu}_2\text{O}\cdot\text{Fe}_2\text{O}_3$ being more stable at higher temperatures. If the B-lines and the lines due to $\text{CuO}\cdot\text{Fe}_2\text{O}_3$

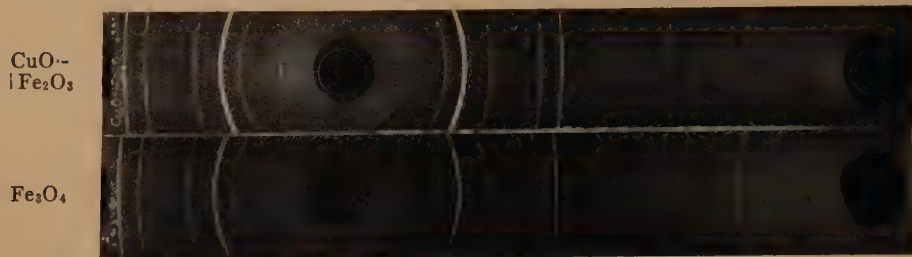


FIG 4—X-RAY DIFFRACTION PATTERN OF $\text{CuO}\cdot\text{Fe}_2\text{O}_3$ COMPARED WITH THAT OF Fe_3O_4
Co radiation (without filter).
 $\text{CuO}\cdot\text{Fe}_2\text{O}_3$ water-quenched from 1000°C .

<i>d</i>	<i>I</i> ^a	<i>B</i>	<i>d</i> -values for Fe_3O_4
4.81	w		4.85
2.96	w-m		2.97
2.86	?		
2.52	vs		2.53
2.41	vw		2.42
2.22	vw		
2.08	w-m		2.10
1.70	w		1.71
1.66	w-vw		
1.60	w-m		1.61
1.512	?-vw		
1.478	m-s		1.483
1.416	??	(1.275) 1.409	
1.337	?		
1.322	?		1.326
1.295	?		
1.275	w		1.279
1.263	?		
1.206	vw		1.210
1.116	vw		1.121
1.088	w-m		1.092
1.048	vw-w		1.049
0.986	vw		0.970
0.966	w		0.966
0.961	?		
0.936	vw		0.940

^as, strong; vs, very strong; w, weak; vw, very weak; ? lines doubtful; ?? lines very doubtful.

42.0 pct copper and 52.7 pct Fe_2O_3 .) The X-ray diffraction pattern of the sample is shown in Fig 5 together with the calculated *d*-values.

The fact that in the X-ray diffraction pattern of the sample ferric oxide lines were absent and $\text{CuO}\cdot\text{Fe}_2\text{O}_3$ lines were present indicated that the sample actually is a mixture of $\text{Cu}_2\text{O}\cdot\text{Fe}_2\text{O}_3$ and $\text{CuO}\cdot\text{Fe}_2\text{O}_3$. This is not surprising because, as Wartman and Thompson have pointed out, cupric ferrite and cuprous ferrite, in the presence of air, could transform into

in the table accompanying Fig 5 are sorted out, the lines remaining should be due to $\text{Cu}_2\text{O}\cdot\text{Fe}_2\text{O}_3$ (see Table 1). These values check very satisfactorily with the published values, which were found after the experiments had been completed and which are given side by side with the above mentioned values, for Delafossite ($\text{Cu}_2\text{O}\cdot\text{Fe}_2\text{O}_3$) as listed (No. II 2294) in the First Supplementary Set of Cards of the Alphabetical Index of X-Ray Diffraction Patterns, published by the American Society for Testing Materials.



FIG 5—X-RAY DIFFRACTION PATTERN OF $\text{Cu}_2\text{O} \cdot \text{Fe}_2\text{O}_3$ (CONTAMINATED WITH SOME $\text{CuO} \cdot \text{Fe}_2\text{O}_3$).
Co radiation; without filter.
Sample cooled by water spray from 1120°C .

d	I	B	$\text{CuO} \cdot \text{Fe}_2\text{O}_3$
4.82	vw		4.81
2.95	w		2.97
2.84	m		
2.76	?-vw	(2.50)2.76	
2.58	w-vw		2.53
2.50	vs		
2.30	?-vw		
2.22	m		
2.08	w		2.10
1.90	?-vw		
1.70	?-vw		1.71
1.65	m		
1.60	w-m		1.60
1.51	m		
1.476	m		1.478
1.426	m		
1.332	w-m		1.326
1.290	w		
1.274	vw		1.279
1.250	vw-w	(1.089)1.203	
1.205	??		1.206
1.180	??		
1.116	w		1.116
1.106	vw		
1.089	vw		1.088
1.046	?-vw		1.048
1.038	w-m		
0.989	w		
0.982	w		
0.966	w-m		0.970
0.951	w		
0.936	w		

The X-ray diffraction patterns of the various synthetic slag samples containing various initial contents of cuprous oxide were also obtained in the same Debye-

Scherrer camera with cobalt radiation. They are given in Figs 6, 7, 8, 9, and 10, together with the calculated d -values for the observed lines.

It is interesting to note that

1. Cuprous oxide lines could not be observed even in slags containing initially as high as 24 pct cuprous oxide. Even in slags with 34.5 pct added initially, the cuprous oxide lines were barely visible.

2. All copper lines showed up clearly, although in slags with very high initial cuprous oxide contents the copper lines were overshadowed by other stronger lines.

3. In slags with initial cuprous oxide contents below 10 pct, the magnetite lines were very distinct.

4. In slags containing higher initial cuprous oxide contents, the $\text{Cu}_2\text{O} \cdot \text{Fe}_2\text{O}_3$ lines gradually became very apparent.

TABLE I—Lines Due to $\text{Cu}_2\text{O} \cdot \text{Fe}_2\text{O}_3$

d	Observed Intensity	d for Delafossite	Intensity I/I_1
2.84	m	2.84	0.7
2.50	vs	2.50	1.0
2.22	m	2.23	0.7
1.65	m	1.66	0.7
1.51	m	1.51	0.7
1.476	m		
1.426	m	1.431	0.6
1.332	w-m	1.336	0.7
1.290	w	1.292	0.5
1.250	vw-w	1.247	0.6w
1.180	??	1.113	0.4w
1.106	vw		
1.089	w	1.080	0.2
1.038	w-m	1.036	0.6w
0.989	w	0.988	0.4w
0.982	w		
0.966	w-m	0.962	0.2w
0.951	w	0.949	0.2w
		0.898	0.4w
		0.853	0.4w
		0.813	0.2w
		0.804	0.4w



FIG 6—X-RAY DIFFRACTION PATTERN OF SLAG CONTAINING INITIALLY 34.5 PER CENT Cu_2O .
Co radiation; without filter.
Sample held at 1200°C for 20 minutes after Cu_2O addition.

d	I	B	$\text{Cu}_2\text{O} \cdot \text{Fe}_2\text{O}_3$	Cu_2O	Cu
4.04	vw				
3.32	vw				
3.13	?-vw				
2.98	?			3.00	
2.84	w-m		2.84		
2.76	?	(2.50)2.76			
2.58	vw				
2.50	s		2.50		
2.46	w	(2.23)2.46		2.45	
2.23	w-m		2.22		
2.11	w			2.12	
2.08	?				2.08
1.89	vw-?				
1.830	??	(1.656)1.830			1.81
1.66	m-w		1.65		
1.613	??				
1.513	m-w		1.51	1.51	
1.432	m-w		1.426		
1.339	w-m		1.332		
1.298	w-vw		1.290		
1.282	w-vw			1.283	1.277
1.254	w		1.250		
1.228	vw	(1.108)1.226		1.228	
1.186	vw		1.180		
1.118	w				
1.108	w		1.106		
1.041	w-m		1.038		1.043
0.992	w		0.989		
0.984	w		0.982		
0.976	?			0.977	
0.966	w		0.966		
0.953	w		0.951	0.953	



FIG 7—X-RAY DIFFRACTION PATTERN OF SLAG CONTAINING INITIALLY 24.0 PER CENT Cu_2O .
Co radiation; without filter.
Sample held at 1200°C for 20 minutes after Cu_2O addition.

d	I	$\text{Cu}_2\text{O} \cdot \text{Fe}_2\text{O}_3$	Cu
4.06	w-vw		
3.34	vw ³		
2.98	vw		
2.84	vw	2.84	
2.52	s	2.50	
2.23	w	2.22	
2.09	w-m		
1.809	vw		2.08
1.715	?		1.81
1.659	vw	1.65	
1.614	vw		
1.513	vw-?	1.51	
1.481	vw-w	1.476	
1.436	vw	1.426	
1.339	vw	1.332	
1.302	vw-?	1.290	
1.275	vw		1.277
1.121	vw		
1.091	w	1.089	1.089
1.042	w-vw	1.038	1.043
0.988	w-vw	0.989	
0.968	w-vw	0.966	
0.951	??	0.951	
0.938	?-vw		

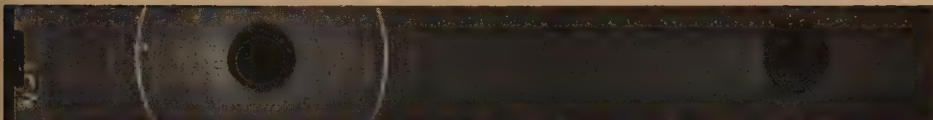


FIG 8—X-RAY DIFFRACTION PATTERN OF SLAG CONTAINING INITIALLY 17.4 PER CENT Cu_2O .
Co radiation; without filter.
Sample held at 1200°C for 20 minutes after Cu_2O addition.

d	I	B	Fe_3O_4	$\text{Cu}_2\text{O} \cdot \text{Fe}_2\text{O}_3$	Cu
4.85	vw		4.85		
4.06	w-m				
3.36	?-vw				
3.14	?	(2.86)3.16			
2.98	w		2.97		
2.86	w			2.84	
2.59	?				
2.53	vs		2.53	2.50	
2.32	?	(2.09)2.31			
2.24	w			2.22	
2.09	w-m		2.10		2.08
1.80	?-vw				1.81
1.71	vw		1.71		
1.66	vw-w			1.65	
1.61	w-m		1.61		
1.482	w-m		1.483	1.51	
1.435	vw			1.426	
1.340	vw			1.332	
1.299	?-vw			1.290	
1.282	vw		1.279		1.277
1.209	?	(1.094)1.210	1.210		
1.123	vw-?		1.121		
1.094	vw-w		1.092	1.089	1.089
1.049	??			1.038	1.043
1.041	?-vw				
0.987	?			0.989	
0.968	vw			0.966	
0.938	?-vw				

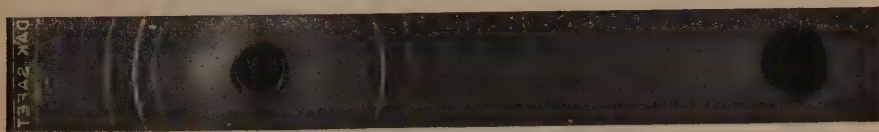


FIG 9—X-RAY DIFFRACTION PATTERN OF SLAG CONTAINING INITIALLY 9.5 PER CENT Cu_2O .
Co radiation (without filter).
Sample held at 1200°C for 20 minutes after Cu_2O addition.

d	I	B	Fe_3O_4	Cu
4.85	?-vw		4.85	
4.46	??			
3.27	?	(2.98)3.29		
2.98	w-m		2.97	
2.79	?	(2.53)2.79		
2.53	vs		2.53	
2.42	??-?		2.42	
2.31	??-?	(2.08)2.30		
2.23	??-?			
2.14	??			
2.08	m-s		2.10	2.08
2.03	?			1.81
1.801	w			
1.758	??			
1.703	vw		1.71	
1.635	?	(1.481)1.638		
1.612	w-m		1.61	
1.431	m		1.483	
1.431	?			
1.440	?			
1.335	?		1.326	
1.322	w-m		1.279	1.277
1.273	?		1.210	
1.212	??	(1.045)1.156		
1.156	?		1.121	
1.123	w-m		1.092	1.089
1.086	?-vw			1.043
1.045	w-vw			
0.967	?			
0.936	?			

MICROSCOPIC EXAMINATION

Polished sections of all the slag samples containing various amounts of cuprous oxide were prepared. Micrographs of these

CHEMICAL ANALYSES

The analysis of slags containing copper oxides was found to be a very difficult task. The total copper content, of course, can



FIG 10—X-RAY DIFFRACTION PATTERN OF SLAG CONTAINING INITIALLY 5 PER CENT Cu_2O .
Co radiation (without filter).
Sample held at 1200°C for 20 minutes after Cu_2O addition.

d	I	B	Fe_2O_3	Cu
4.85	vw		4.85	
4.05	s			
3.33	vw			
3.13	?-vw			
2.94	w-m			
2.84	?	(2.52)2.79	2.97	
2.69	vw			
2.52	vs		2.53	
2.41	??		2.42	
2.09	m		2.10	2.08
1.81	??			1.81
1.71	vw		1.71	
1.69	??			
1.61	m-s		1.61	
1.478	s-m		1.486	
1.368	??			
1.324	??		1.326	
1.276	w		1.279	1.277
1.264	??			
1.206	vw-?	(1.090)1.206	1.210	
1.118	v-vw		1.121	
1.090	vw-m		1.092	1.089
1.048	vw-w		1.049	1.043
0.987	vw			
0.968	w		0.970	
0.938	vw		0.940	

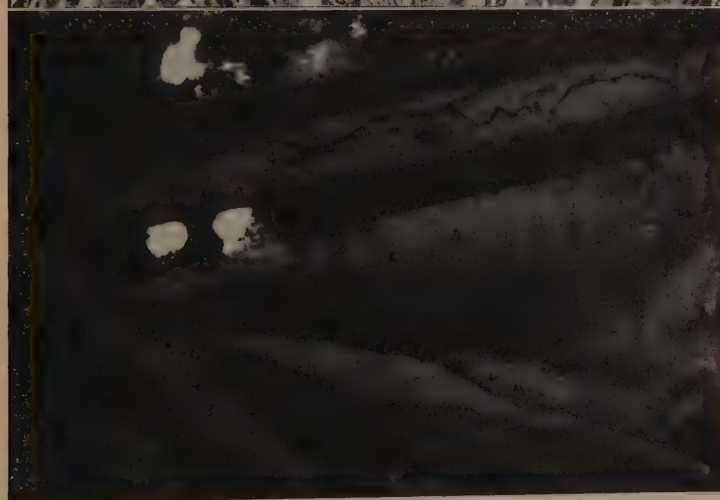
specimens are shown in Figs 11 to 21. The isometric magnetite structures as dendrites can be easily recognized in samples with comparatively low initial cuprous oxide concentrations as shown in Figs 18, 19, 20, and 21. Metallic copper is clearly visible in almost all the samples as bright oval spots. In samples with initial cuprous oxide contents higher than 10 pct, the needle-like crystals of $\text{Cu}_2\text{O}\cdot\text{Fe}_2\text{O}_3$ begin to appear. The microstructure of the impure cuprous ferrite, etched with 6 pct nital, is shown in Figs 22 and 23. It is clear that the needle-like structure is similar to those found in slag samples containing high initial cuprous oxide contents.

be known with great accuracy. However, the copper in the slags might be present as metallic copper, cuprous or cupric ferrite, or cuprous oxide. The amount of copper as ferrite can be known, because very fortunately cuprous ferrite was found to be insoluble in potassium cyanide solution.⁶ By the difference from the total, the amount of copper as metal and as oxide can be known, but no satisfactory way could be found to differentiate oxide copper from metallic copper in the slags, because the metallic copper present was so fine that it would dissolve in all reagents that dissolved cuprous oxide.

The analysis of ferrous and ferric iron that ordinarily would have no difficulty



11



12

FIGS. 11 AND 12—SLAG CONTAINING INITIALLY 34.5 PER CENT Cu_2O .Fig 11 shows $\text{Cu}_2\text{O}\cdot\text{Fe}_2\text{O}_3$ needles. $\times 250$.Fig 12 shows $\text{Cu}_2\text{O}\cdot\text{Fe}_2\text{O}_3$ needles and some bright metallic copper particles. $\times 2000$.

at all now became a problem that could not be solved satisfactorily. The total iron can be known easily from analytical determinations, but the amount of ferrous or ferric iron could not be known with any accuracy, because when the samples were put into solution in acids, the cuprous ions would reduce the ferric ions, so that the results obtained would be unreliable and useless. In Table 2, therefore, only the total copper, copper as ferrites, ratio of copper in ferrites to total copper, and

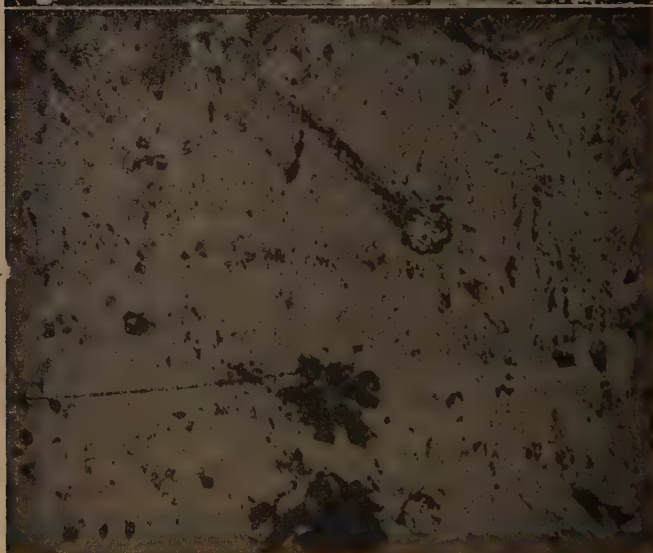
TABLE 2—Chemical Analyses
PER CENT

Slag	Initial Cu_2O Added	Total Cu Found	Copper as Cu Ferrites	Ratio Ferrites to Total	Total Iron
A	34.5	29.89	22.40	0.75	24.21
		30.12	23.18	0.77	24.06
B	24	20.62	14.10	0.68	27.52
		20.79	13.30	0.64	27.10
C	17.4	15.05	5.20	0.29	30.21
		15.13	4.57	0.30	30.61
D	9.5	8.18	0.76	0.09	32.60
		8.18	0.89	0.11	33.40
E	5.0	4.18	0.42	0.10	34.80

13



14

FIGS 13 AND 14—SLAG CONTAINING INITIALLY 24 PER CENT Cu_2O .Fig 13 shows $\text{Cu}_2\text{O}\cdot\text{Fe}_2\text{O}_3$ needles. $\times 250$.Fig. 14 shows $\text{Cu}_2\text{O}\cdot\text{Fe}_2\text{O}_3$ needles, metallic copper, and magnetite-like crystals. $\times 250$.

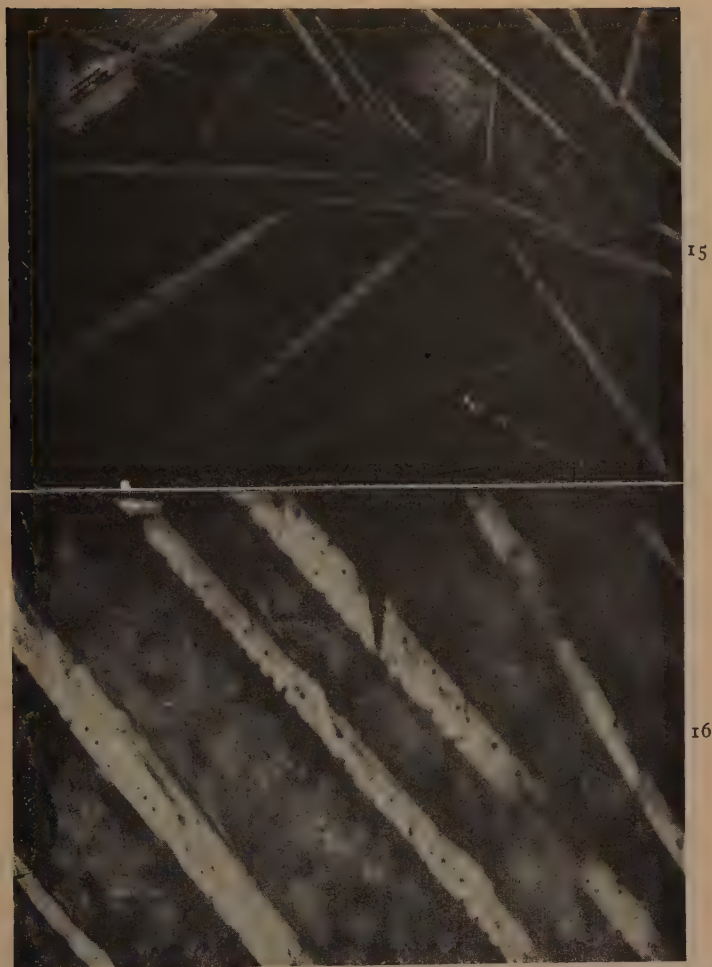
total iron content are given, without any values for the metallic copper content, the cuprous oxide content, and the magnetite content.

The low copper content as ferrites indicates that the strong magnetite lines in the X-ray diffraction patterns of these

two slag samples were due primarily to magnetite and not to cupric ferrite, which gives a very similar X-ray diffraction pattern.

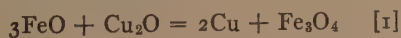
THERMODYNAMIC CALCULATIONS

The absence of cuprous oxide and the presence of copper and magnetite together



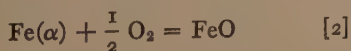
FIGS 15 AND 16—SLAG CONTAINING INITIALLY 24 PER CENT Cu_2O , SHOWING $\text{Cu}_2\text{O} \cdot \text{Fe}_2\text{O}_3$ NEEDLES. $\times 2000$.

as shown by the X-ray investigations and microscopic examinations suggest immediately that the reaction

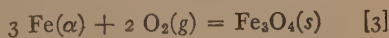


might have taken place. Thermodynamic calculation therefore was made of the free energy change of the reaction.

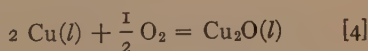
From data compiled by Kelly,⁷ the standard free energy change for the reaction



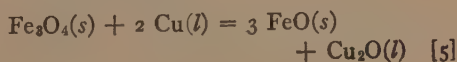
was given. From this and from the free energy changes of the reaction⁷



and of the reaction⁷



we can calculate the free energy change for the reaction



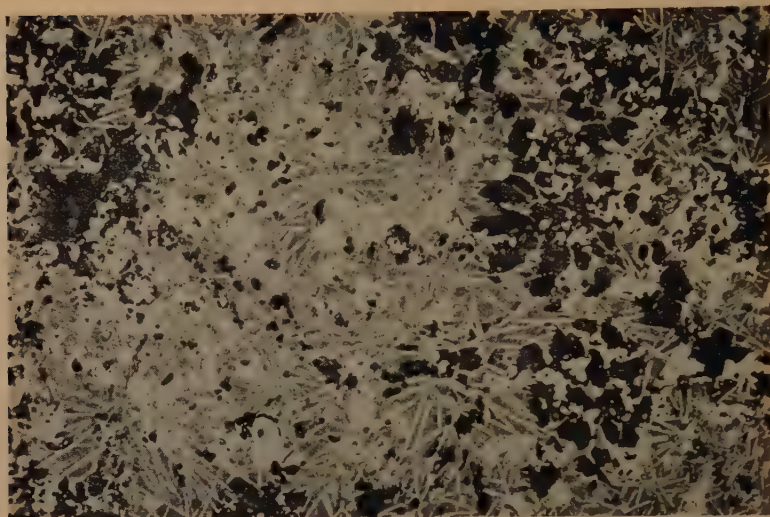


FIG 17—SLAG CONTAINING INITIALLY 17.4 PER CENT Cu_2O , SHOWING $\text{Cu}_2\text{O}\cdot\text{Fe}_2\text{O}_3$ NEEDLES, METALLIC COPPER, AND MAGNETITE-LIKE AREAS. $\times 250$.

as follows:

$$\begin{aligned}
 [3] \times [2] \quad \Delta F^\circ &= -185810 - 30.06T \log T + 7.53 \times 10^{-3}T^2 - 0.264 \times 10^5T^{-1} + 135.54T \\
 [3] \quad \Delta F^\circ &= -272540 - 28.19T \log T + 0.42 \times 10^{-3}T^2 + 3.020 \times 10^5T^{-1} + 167.74T (- \\
 &\quad \Delta F^\circ = -86730 - 1.87T \log T + 7.11 \times 10^{-3}T^2 - 3.284 \times 10^5T^{-1} - 32.20T \\
 [4] \quad \Delta F^\circ &= -36590 - 11.19T \log T + 0.06 \times 10^{-3}T^2 - 0.469 \times 10^5T^{-1} + 48.43T (+ \\
 &\quad \Delta F^\circ = -50140 - 13.06T \log T + 7.17 \times 10^{-3}T^2 - 3.753 \times 10^5T^{-1} + 16.63T
 \end{aligned}$$

By substituting temperatures in this equation, we can calculate the free energy change of the reaction at different temperatures as shown in Table 3.

TABLE 3—Calculated Free Energy Changes at Different Temperatures for Reaction $\text{Fe}_2\text{O}_4(s) + 2\text{Cu}(l) = 3\text{FeO}(s) + \text{Cu}_2\text{O}(l)$

T , Deg K	ΔF°	Log K
1200	31800	-5.97
1300	30050	-5.15
1400	29060	-4.62
1473	28970	-4.30
1500	28750	-4.10
1600	26560	-3.63

log K was calculated from the equation

$$F^\circ = -RT \ln K$$

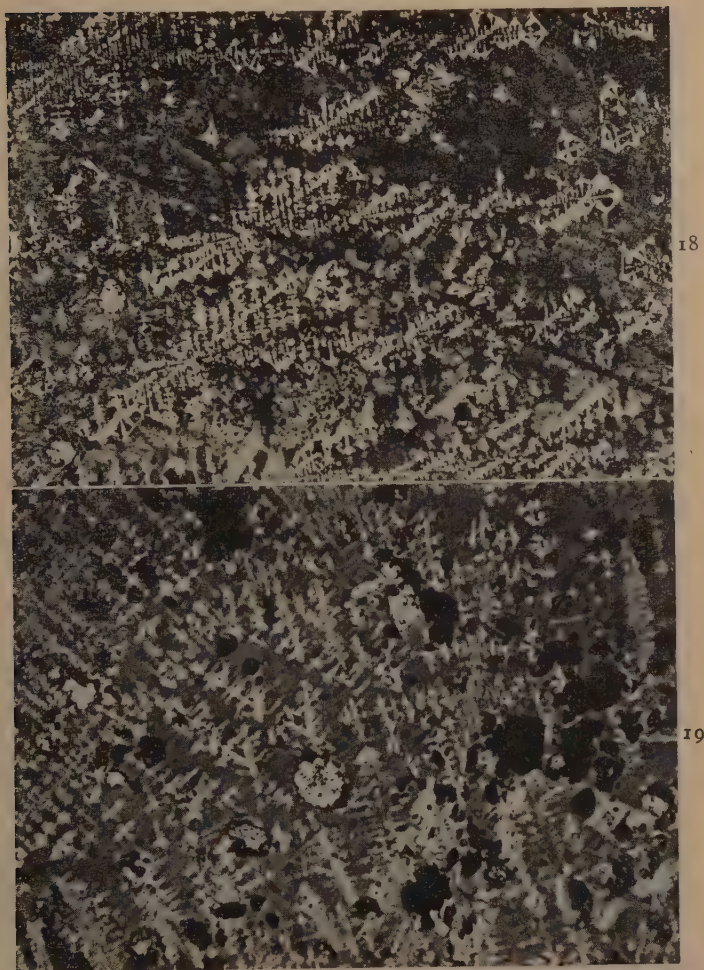
At the temperatures used (1200°C), log $K = -4.30$ or $K = 5.0 \times 10^{-5}$. This shows that at 1200°C there is a strong

tendency for the reaction to go to completion toward the left. Now

$$K = \frac{a^3_{\text{FeO}(s)} \cdot a_{\text{Cu}_2\text{O}(l)}}{a^2_{\text{Cu}(l)} \cdot a_{\text{Fe}_2\text{O}_4(s)}} \quad [V 6]$$

where $a_{\text{FeO}(s)}$, $a_{\text{Cu}_2\text{O}(l)}$, $a_{\text{Cu}(l)}$ and $a_{\text{Fe}_2\text{O}_4(s)}$ are the activities of $\text{FeO}(s)$, $\text{Cu}_2\text{O}(l)$, $\text{Cu}(l)$ and $\text{Fe}_2\text{O}_4(s)$, respectively. The solubility of metallic copper in slags is negligible, and if we further assume that the copper is nearly a pure liquid, the activity of $\text{Cu}(l)$ can be assumed to be unity. Similarly, the activity of solid magnetite, which, having a very high melting point, would probably be separated from the slag system as a solid phase as soon as it is formed, can be assumed to be unity; so Eq 5 becomes

$$K = a^3_{\text{FeO}(l)} \cdot a_{\text{Cu}_2\text{O}(l)} \quad [7]$$



FIGS 18 AND 19—METALLIC COPPER PARTICLES AND DENDRITIC MAGNETITE STRUCTURES. $\times 250$

Fig 18, slag containing initially 17.4 per cent Cu_2O .

Fig 19, slag containing initially 9.5 per cent Cu_2O .

The isoactivity lines of FeO in slags of the system $\text{SiO}_2\text{-FeO-CaO}(+\text{MgO})$ have been shown by C. R. Taylor and J. Chipman⁵ to deviate considerably from the constant FeO lines in the ternary system. Fortunately, however, on the acid side, the deviation is much less pronounced, so it may be assumed that the activity of FeO in copper reverberatory slags is roughly equal to the mol fraction of FeO in slag, which is about 0.4.

Let it be assumed that the activity of

cuprous oxide in the slags approximately equals its mol fraction. Then

$$\begin{aligned} K &= (0.4)^3 \times a_{\text{Cu}_2\text{O}} \\ \therefore a_{\text{Cu}_2\text{O}} &= \frac{5 \times 10^{-5}}{6.4 \times 10^{-2}} \\ &= 7.8 \times 10^{-4} \end{aligned}$$

This means that the cuprous oxide finally left is vanishingly small. However, this happened only at the very beginning of the reaction. As soon as the reaction started, one mol of cuprous oxide reacted will

20



21

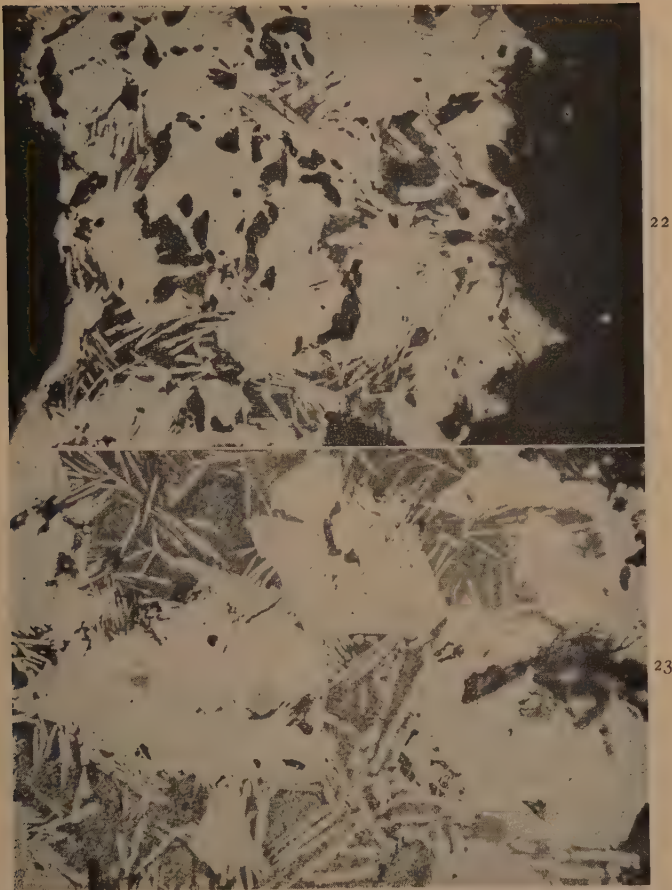


FIGS 20 AND 21—SLAG CONTAINING INITIALLY 5 PER CENT Cu_2O .
 Fig 20 shows magnetite and metallic copper particles. $\times 250$.
 Fig 21 shows dendritic magnetite structure. $\times 2000$.

remove three mols of FeO . The concentration of FeO will decrease sharply, and the final concentration of cuprous oxide tends to increase, in order to satisfy Eq 7. Let A be the mol fraction of cuprous oxide introduced and B the mol fraction of cuprous oxide left after equilibrium. Since one mol of cuprous oxide will react and remove three mols of FeO ,

$$K = 5.0 \times 10^{-5} \\ = [0.4 - 3(A - B)]^3 \cdot B \quad [8]$$

Of course, when A is large, it will affect the activity of FeO appreciably from dilution effects alone. In other words, the initial concentration of FeO is actually a function of A and should not be considered as a constant. For simplicity in

FIGS 22 AND 23—CUPROUS FERRITE ($\text{Cu}_2\text{O} \cdot \text{Fe}_2\text{O}_3$). NITAL ETCHED.Fig 22, $\times 250$.Fig 23, $\times 500$.

calculation, the initial concentration of FeO may be taken as a constant.

By trials, Eq 8 can be solved (Table 4).

TABLE 4—Solution of Equation 8

A	B	B/A
0.001	0.00079	0.79
0.01	0.00096	0.096
0.025	0.0014	0.059
0.05	0.003	0.060
0.10	0.016	0.160
0.15	0.050	0.333
0.20	0.141	0.470

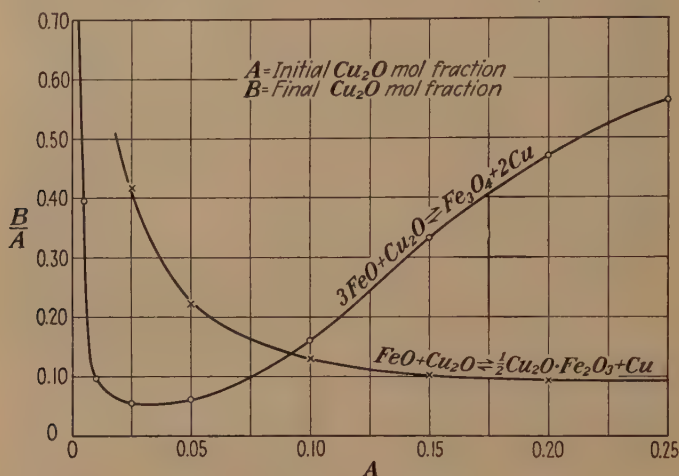
In Fig 24 the B/A ratios were plotted against A , $A = 0.025$, roughly correspond-

ing to the slag sample with 5 pct initial Cu_2O , $A = 0.05$ roughly to the slag with 9.5 pct initial Cu_2O , $A = 0.1$ roughly to slag with 17.4 pct initial Cu_2O , $A = 0.15$ roughly to slag with 24 pct initial Cu_2O , and $A = 0.20$ roughly to slag with 34.5 pct initial Cu_2O . (To be more exact, a slag sample with initial content of 5 pct Cu_2O corresponds to $A = 0.023$; that with initial content of 9.5 pct Cu_2O corresponds to $A = 0.046$; that with initial content of 17.4 pct Cu_2O corresponds to $A = 0.093$; that with initial content of 24 pct Cu_2O corresponds to $A = 0.125$; that

with initial content of 34.5 pct Cu_2O corresponds to $A = 0.192$.)

The fact that Fe_3O_4 and Cu lines were so prominent in the diffraction pictures

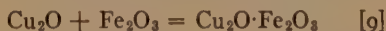
Unfortunately, the thermodynamic properties of $\text{Cu}_2\text{O} \cdot \text{Fe}_2\text{O}_3$ are entirely unknown and no direct calculation of free energy change of any accuracy can be made.



FIG—24, RATIO OF B/A TO A .

of the slag samples with initial cuprous oxide content lower than 10 pct can be easily explained, because, as shown in the figure, about 90 to 95 pct of the initial cuprous oxide will have reacted with the ferrous oxide in the slags to form magnetite and metallic copper. As the initial cuprous oxide content increases, a higher percentage of cuprous oxide will be left.

The formation of $\text{Cu}_2\text{O} \cdot \text{Fe}_2\text{O}_3$ may either be from the reaction of Cu_2O with the ferric ion already present in the slag,



or from the reaction of Cu_2O with the magnetite formed, as



which, when combined with the reaction



gives $2\text{Cu}_2\text{O} + 2\text{FeO}$



i.e., $\text{Cu}_2\text{O} + \text{FeO}$

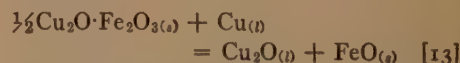


However, from X-ray and microscopic evidence, and from chemical analysis, very little $\text{Cu}_2\text{O} \cdot \text{Fe}_2\text{O}_3$ was present in samples with low initial Cu_2O content; this means that at the beginning of reaction 12, the equilibrium constant must be such that, for the same initial concentration of FeO , the concentration of Cu_2O left must be greater than 0.00079 mol fraction, which is the maximum amount of Cu_2O that can exist with the initial amount of FeO according to the reaction



at 1200°C .

Now, the equilibrium constant for the reaction



can be expressed by the following equation:

$$K = \frac{a_{\text{Cu}_2\text{O}(l)} a_{\text{FeO}(s)}}{a_{\frac{1}{2}\text{Cu}_2\text{O} \cdot \text{Fe}_2\text{O}_3(s)} a_{\text{Cu}(l)}} \quad [14]$$

Assuming unity activity for $\text{Cu}_2\text{O} \cdot \text{Fe}_2\text{O}_3(s)$ and for $\text{Cu}(l)$, we get

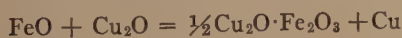
$$K = a_{\text{Cu}_2\text{O}(l)} a_{\text{FeO}(s)} \quad [15]$$

In this reaction, one mol of Cu_2O reacted to form $\text{Cu}_2\text{O} \cdot \text{Fe}_2\text{O}_3$, removed only one mol of FeO , and the equilibrium constant depends on the first power of the activity instead of on the third power as in Eq 7. By reasoning similar to that for reaction 13,

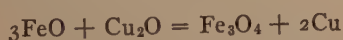
$$K = [0.4 - (A - B)]B \quad [16]$$

where A is the initial Cu_2O mol fraction of the slag and B is the final Cu_2O mol fraction left.

By solving Eq 16 for B , it was found that B increased steadily as A increased, but with a rate much slower than in the case for Eq 8, so that if the ratio B/A is plotted against A as in Fig 24, the curve decreased steadily up to $A = 0.25$. The exact position of the curve depends on the equilibrium constant K . Although we do not know K exactly, it must be such that the curve for



will intersect the curve for



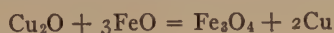
near the point $A = 0.1$, because very little $\text{Cu}_2\text{O} \cdot \text{Fe}_2\text{O}_3$ exists when A is below 0.1. This limits the order of magnitude of K to about 0.004, for which the B values can be calculated at various A values as in Table 5.

TABLE 5—Calculation of B Values

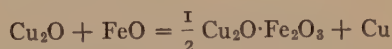
A	B	B/A
0.025	0.0104	0.416
0.05	0.0111	0.222
0.10	0.0128	0.128
0.15	0.0151	0.101
0.20	0.0183	0.0195
0.25	0.0231	0.0925

A comparison of these values with those listed in Table 4 shows clearly that at low initial cuprous oxide con-

centration B is much lower for the reaction



than the reaction

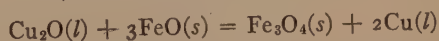


At high initial concentrations of cuprous oxide, the reverse becomes true. This means that at low initial concentrations of cuprous oxide magnetite formation will be predominant, whereas at high initial concentrations of cuprous oxide ferrite formation becomes important. The two curves met at $A = 0.09$, which is the point at which both reactions should go on with approximately equally strong tendency. This explains clearly how and why in the X-ray diffraction pictures the $\text{Cu}_2\text{O} \cdot \text{Fe}_2\text{O}_3$ became gradually stronger as initial cuprous oxide concentration increased.

CONCLUSIONS

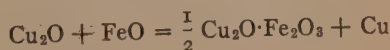
1. When cuprous oxide is added to copper reverberatory slags at high temperature (1200°C) reaction between cuprous oxide and ferrous oxide in the slag will set in.

2. If the initial cuprous oxide content is low, the reaction



will be predominant, so that the resultant slags will be high in magnetite and metallic copper.

3. If the initial cuprous oxide content is high, the reaction



will take place.

4. Appreciable amounts of free cuprous oxide can be present in reverberatory slags only with extremely high initial concentrations of Cu_2O when most of the FeO in the slags has been removed by the reactions shown herein. In other words, under equilibrium conditions appreciable

amounts of free Cu_2O cannot be present in copper reverberatory slags under ordinary circumstances.

ACKNOWLEDGMENTS

The authors wish to express their gratitude to Prof. John Chipman, who made available to them the facilities of the Steel-Making Laboratory of the Massachusetts Institute of Technology and gave many valuable suggestions; to Prof. John T. Norton and Prof. Daniel Rosenthal for their kind help in some of the X-ray work; and to Prof. N. J. Grant for his valuable technical assistance during the experiments.

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The Oxidation of Chalcocite in Air Compared with Its Oxidation in Pure Oxygen

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(New York Meeting, February 1948)

RECENTLY there has been much speculation concerning the advantages of using oxygen enriched air or pure oxygen in pyrometallurgical processes. The advantage of using oxygen in the iron blast furnace and elsewhere in ferrous production metallurgy has been given careful consideration and, as a result, several experiments have been tried and a number of papers have recently appeared on this subject.^{1,2} The use of oxygen in nonferrous smelting likewise poses interesting problems, therefore any experimental data obtained in this area should likewise be of general interest.³ Ashcroft⁴ in 1933 claimed to have obtained improved results when copper concentrates were roasted in pure oxygen. However, his paper gives neither data nor experimental details.

A few years ago a research program was started in this laboratory which had for its objective the determination of the mechanism of oxidation of metallic sulphides under varying conditions. To date we have studied the oxidation of galena,⁵ sphalerite, and chalcocite.

It is a well known fact that copper sulphide minerals are oxidized slowly by

weathering agents, so that the sulphides of copper which find their way into a tailing pond are gradually changed into water-soluble and acid-soluble compounds. Commercially, the oxidation of copper sulphide minerals is accomplished by roasting them at elevated temperatures in air using a suitable (usually multiple hearth) roaster. Most copper smelters are equipped with such roasters.

In this phase of the study we were especially interested in determining the effect of temperature on: (1) the air oxidation of chalcocite and (2) the oxidation of chalcocite using commercial oxygen. The amount of sulphur removed as sulphur dioxide, the percentages of water-soluble copper, and of acid-soluble copper were determined for the air oxidation tests. In the tests using commercial oxygen, the percentages of sulphur dioxide, water-soluble copper, acid-soluble copper, water-soluble sulphur and acid-soluble sulphur were determined. For these experiments the temperature was varied from 250 to 700°C.

EXPERIMENTAL

Preparation of Chalcocite (Cu₂S)

Natural chalcocite is not pure. Minerals such as bornite, covellite, and chalcophyllite may be present. It was decided, therefore, to prepare some chalcocite in our own laboratory.

An intimate mixture of sulphur and finely divided metallic copper in the ratio of 4 g of copper to 1 g of sulphur was prepared. To this was added a slight excess of

Manuscript received at the office of the Institute November 17, 1947. Issued as TP 2388 in METALS TECHNOLOGY, June 1948.

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¹ References are at the end of the paper.

sulphur to take care of the oxygen known to be present in the powdered copper.

A size 3 Coors porcelain crucible *A* (Fig 1) containing the mixture of copper and

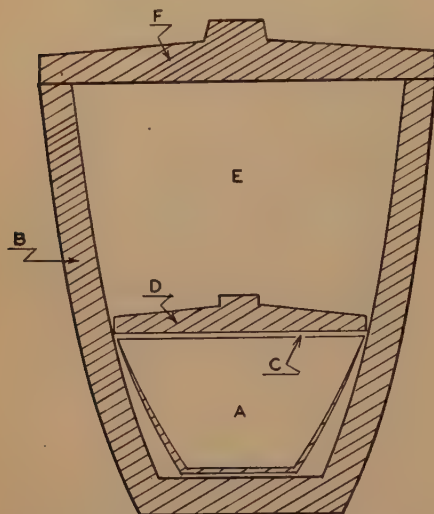


FIG 1—APPARATUS FOR PREPARATION OF SYNTHETIC CHALCOCITE.

sulphur was placed in a 30 g assay crucible *B* and covered with a sheet of mica *C*. On top of this sheet was placed a suitable fire clay cover *D* and above this bone ash was packed *E*. Finally another fire clay cover was placed tightly on the fire assay crucible *F*. This simple apparatus gave a product that compared very favorably with that prepared by Posnjak, Allen and Merwin⁶ in the bomb type apparatus developed by Allen, Crenshaw, Johnston, and Larsen.⁷

Chalcocite melts⁶ at 1130°C. To obtain temperatures within this range, a pot furnace heated by natural gas was used. It was found by trial that the charge was completely fused by holding the temperature near 1140°C for 2 hr.

The product had the ordinary appearance of natural chalcocite and a microscopic examination of a polished specimen showed it to be homogeneous with a typical slate-gray color. An X ray analysis of a sample performed by Prof. Dan McLachlan

of our metallurgy staff indicated that it had a structure identical with that of natural chalcocite.

The assay on this material showed that the percentage of copper and sulphur was low, indicating that probably some copper oxide was present. Accordingly, the entire batch of prepared chalcocite was ground to -100 +200 mesh and leached for 48 hr with dilute (1 to 10) hydrochloric acid. The leached sample was carefully washed in distilled water and then dried in an atmosphere of nitrogen. To prevent subsequent oxidation, it was stored in a container in an atmosphere of nitrogen.

Posnjak and Allen's synthetic chalcocite contained an excess of sulphur, caused, probably, by the formation of some cupric sulphide giving a solid solution of cupric sulphide in cuprous sulphide. The assay of our leached chalcocite indicates we had very little, if any, excess sulphur present. Typical results are:

Assay	Pct Cu	Pct S
1	79.9	20.08
2	79.8	20.08
3	79.8	19.96
4	79.85	20.06
Theoretical	79.87	20.13

Apparatus and Preliminary Experiments

A sketch of the apparatus used in these experiments is given in Fig 2. The arrangement is similar to that used by other investigators for tests of this type. Oxidation tests were performed in the 1 × 30-in. glazed porcelain tube *A* which was heated in a multiple unit electric furnace *B*, the temperature of which could be varied by adjustment of a "Varitran" variable transformer. A charge of 1 g of synthetic chalcocite was spread evenly over the bottom of a 3-in. glazed porcelain boat *C* and this was placed in the centre of the furnace.

The temperature was measured on a Brown potentiometer *D* with a chromel-

alumel thermocouple *E*, the tip of which was supported over the centre of the boat by means of a porcelain block *F*.

The air or industrial oxygen was dried by passing it through concentrated sulphuric

determined gravimetrically as barium sulphate.

In some preliminary results obtained using air as the oxidant, it was found that the yield of the various products was not

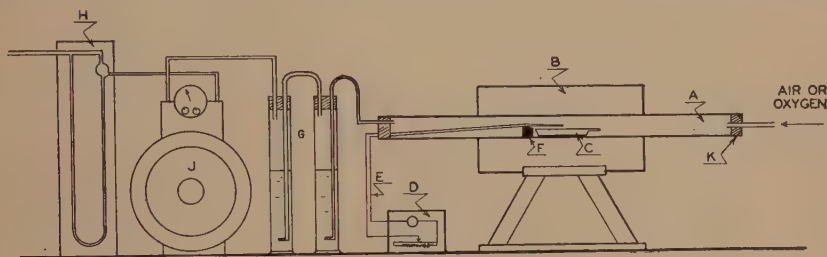


FIG 2—OXIDATION APPARATUS.

- | | | |
|---------------------|--------------------|----------------------|
| A. Porcelain tube | D. Potentiometer | G. Absorption towers |
| B. Electric furnace | E. Thermocouple | H. Flowmeter |
| C. Porcelain boat | F. Porcelain block | J. Gas meter |

acid and then through anhydrous calcium chloride. The exit gases passed through glass tubing joined where necessary with rubber, and into the absorption towers *G* which contained sintered glass discs to cause high dispersion of the gas. The flow of gas was measured by a simple U-tube flow meter *H* and a gas meter *J*; the volume of air or oxygen could thus be quickly adjusted to the required number of cubic feet per hour.

Absorption of sulphur dioxide was effected in towers *G* by a 10 pct iodine solution for the tests with air. Excess of iodine over that necessary to react with the sulphur dioxide was titrated with standard sodium thiosulphate using starch as indicator. This method seemed to give erratic results in the tests using oxygen at high temperatures where chalcocite oxidized very rapidly. Consequently, a 3 pct solution of hydrogen peroxide was used in the absorption towers *G* to oxidize the sulphur dioxide to sulphate ion ($\text{SO}_4 =$). This was precipitated and weighed as barium sulphate. Although this method was more tedious than simple absorption in iodine, it proved to be more dependable.

Soluble copper was determined by the standard iodide-thiosulphate method. For the tests with oxygen, soluble sulphur was

very sensitive to the rate at which the gas was passed over the heated chalcocite, except at 450°C . At this temperature there was a marked increase in the production of water soluble copper when the volume of air was reduced from 1 to $\frac{1}{2}$ cfhr. It was also found that the time of treatment was a variable and needed to be established. Table 1 presents the data obtained.

TABLE 1—*The Effect of Rate of Gas Flow at Various Temperatures, and Also the Effect of Time at 450°C on the Yield of Water Soluble Copper*

Temperature of Run, $^\circ\text{C}$	Time of Run in Minutes	1 Cfhr Air Pct Soluble Copper	0.5 Cfhr Air Pct Soluble Copper
250	60	0.22	0.00
300	60	0.27	0.00
350	60	1.95	1.71
400	60	6.51	7.77
450	60	11.26	32.27
400	60		22.08
550	60	8.21	8.35
650	60	0.00	1.34
450	15		4.07
450	30		7.51
450	45		32.29
450	60		32.78
450	75		32.68

On the basis of the information in Table 1 it was decided to use $\frac{1}{2}$ cfhr of air or oxygen (which is 236 cc per min.) and to hold the time at 1 hr for each run where air was used and at 2 hr where oxygen was used.

Experimental Results

The data obtained are tabulated in Tables 2 and 3 and are shown graphically in Fig 3, 4, 5, and 6.

DISCUSSION OF RESULTS

An examination of Table 2 and Curve A in Fig 3 where air is the oxidant shows the change in the percentage of water-soluble

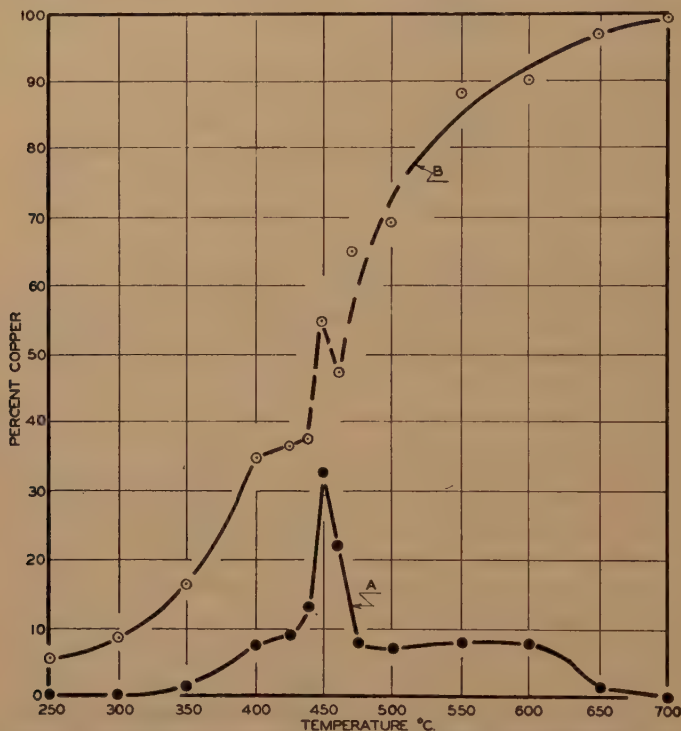


FIG 3—OXIDATION OF CHALCOCITE IN AIR AT VARIOUS TEMPERATURES.

A. Water-soluble copper
B. Acid-soluble copper

TABLE 2—Oxidation of Chalcocite in Air at Various Temperatures (1 g Chalcocite used in Each Determination)

Run No.	Temperature °C	Per Cent Sulphur as SO ₂	Per Cent Water-soluble Copper	Per Cent Acid-soluble Copper	Per Cent Total Soluble Copper
1	250	1.99	0.00	5.43	5.43
2	300	4.47	0.00	8.54	8.54
3	350	6.54	1.71	16.67	18.38
4	400	8.95	7.77	35.03	42.80
5	425	9.20	8.95	36.45	45.40
6	440		13.10	36.87	49.97
7	450 ^a	24.38	32.27 ^a	54.84	87.11
8	460 ^b		22.08	47.70	69.78
9	475	54.48	7.61	65.01	72.62
10	500	63.68	7.02	69.39	76.41
11	550	76.72	8.35	88.25	96.60
12	600	79.80	7.48	89.96	97.44
13	650	92.54	1.34	96.98	98.32
14	700	98.26	0.00	99.11	99.11

^a Other results for per cent water-soluble copper formed at 450°C were: 32.29, 32.78, 32.68 and 33.60 pct copper.

^b Fusion occurred with "boiling."

copper obtained with increase of temperature. Thus at 350°C only 1.71 pct of the chalcocite copper has become water-soluble. This solubility increased sharply until at 450°C the water-soluble copper reaches a value of 32.27 pct. As will be observed, the soluble copper falls off sharply at temperatures above 450°C. For example at 475°C the percentage of water-soluble copper is only 7.61 pct. Curve B, Fig 3 represents the acid-soluble copper formed from the chalcocite. In general the percentage of acid-soluble copper, which probably is oxides and basic sulphates,*

* In the air oxidation of chalcocite, no attempt was made to determine basic copper sulphate. No doubt it was formed in the temperature range 350 to 600°C.

increased with temperature until, at 700°C, all the chalcocite copper has been converted to acid-soluble forms. It is interesting to observe that a "jog" in curve *B* comes at

of soluble copper begins at about 300°C and increases to a maximum at 450°C where the amount of water-soluble copper obtained is approximately 42 pct of the

TABLE 3—Oxidation of Chalcocite in Oxygen at Various Temperatures (1 g of Chalcocite Used in Each Determination)

Run No.	Temperature °C.	Per Cent Sulphur as SO ₂	Per Cent Water-soluble Copper	Per Cent Acid-soluble Copper	Per Cent Total Soluble Copper	Per Cent Water-soluble Sulphur	Per Cent Acid-soluble Sulphur	Per Cent Total Soluble Sulphur
15	250	10.82	0.11	12.34	12.45			
16	300	11.53	0.70	23.36	24.06			
17	300					0.73	0.60	
18	350		2.38	30.52	32.90			
19	350	13.89	2.17	28.22	30.39			
20	400		7.84	41.78	49.62			
21	400	16.65	7.04	36.82	43.86			
22	400			38.30		10.53	6.08	
23	410		9.50	32.47	41.97			
24	410	14.38	7.85	27.32	35.17			
25	420		10.60	40.11	50.71			
26	420	17.88	9.48	30.85	40.33			
27	430		11.27	35.34	46.61			
28	430	16.46	17.78	41.07	58.85			
29	440		26.07	44.08	70.15			
30	440	17.59	17.04	37.01	54.05			
31	450		41.64	55.20	96.80			
32	450		37.25	59.79	97.04			
33	450	21.34	38.01	60.79	98.80			
34	450	21.45	32.33	47.85	80.18	79.69	8.97	
35	450		40.22	57.89	98.11			
36	460		37.51	61.27	98.78			
37	460	20.86	38.11	61.10	99.21			
38	470		30.06	66.85	97.81			
39	470	29.13	32.85	66.46	99.31			
40	480		18.44	76.32	94.76			
41	480	28.06	31.20	66.70	97.90			
42	480	32.20	26.81	70.50	97.31	53.53	7.75	93.48
43	490		11.84	77.60	89.44			
44	490	43.75	20.82	77.14	97.96			
45	500		17.02	81.75	98.77			
46	500		16.73	73.39	90.12			
47	500	54.69	19.91	78.35	98.26	39.30	8.83	102.82
48	550		9.23	85.65	94.88			
49	550		6.00	91.69	97.69			
50	550	60.31	9.79	80.95	90.74	20.06	16.68	97.05
51	600		8.16	89.92	98.08			
52	600		7.57	90.66	98.23			
53	600		9.31	90.84	100.15	19.98	15.00	
54	600		8.11	90.31	98.42	16.96	20.55	
55	600				98.36			
56	600	67.74	8.64	87.70	96.34	17.65	15.88	101.27
57	650		7.50	90.53	98.03			
58	650		7.31	87.83	95.14	15.88	17.39	
59	650	68.76		91.40		14.30	14.48	97.54
60	700		5.98	91.84	97.82			
61	700		6.69	91.62	98.31	14.40	21.10	
62	700		7.44	90.84	98.28	15.59		
63	700				98.89	8.12	28.60 ^a	
64	700	77.62					12.99	98.73

^a Combined water- and acid-soluble sulphur.

Fusion was observed from Tests 21 to 51, inclusive.

Beginning with run 42, sulphur dioxide was determined by oxidizing it with hydrogen peroxide. The sulphate formed was precipitated as barium sulphate and weighed.

the temperature where fusion begins (450°C). This will be considered later.

Fig 4 shows that the curves for the oxidation of chalcocite in oxygen are similar in form to those for oxidation in air. Considering curve *A*, Fig 4, the formation

copper in the sample. This is a much better yield than that obtained using air at 450°C. Also by using oxygen in place of air, it appears that more soluble copper is produced at temperatures between 450 and 700°C. Apparently the decomposition tem-

perature of copper sulphate is dependent on the experimental conditions. It is of interest to note that values reported in the literature⁸ vary from 650 to 740°C.

These reactions produce metallic copper (which is not readily soluble in a dilute hydrochloric acid solution), at the expense of acid-soluble copper oxides. The authors

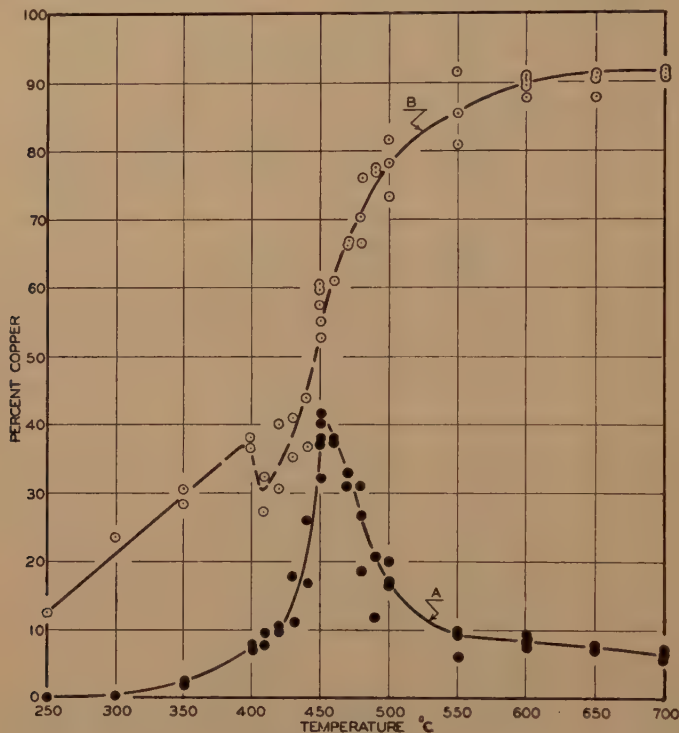
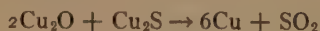


FIG 4—OXIDATION OF CHALCOCITE IN OXYGEN AT VARIOUS TEMPERATURES.

A. Water-soluble copper
B. Acid-soluble copper

The jog in curve *B* Fig 4 comes at about 400°C rather than at 450°C as was the case in Fig 3. But here, as before, the jog occurs where fusion begins. The experimental points in this fusion zone are somewhat scattered and therefore the existence of a jog may be questioned. To emphasize this uncertainty we have drawn broken line curves through these areas. For example, it does not seem likely that there should be less acid-soluble copper at 415 than at 400°C, unless reactions such as the following take place:



re-examined some of the fused material to determine whether or not metallic copper was present. Three tests were made. In the first one some fused material was quenched in cold water and then made part of a bakelite briquette. In the second test the fused material was allowed to cool in air and then briquetted as before. In the third test the fused material was cooled, leached in dilute hydrochloric acid for 36 hr and then briquetted. The three samples thus prepared were examined with a microscope and the presence of metallic copper was observed in each.

In the results for the conversion of chalcocite sulphur into other compounds of

sulphur, a marked difference is observed between tests with air and with oxygen. Fig 5, curve B shows how the evolution of sulphur dioxide increased greatly at 425°C,

cated the presence of cupric sulphate (CuSO_4).

Sulphur determinations on the acid-soluble products showed that the chalcocite

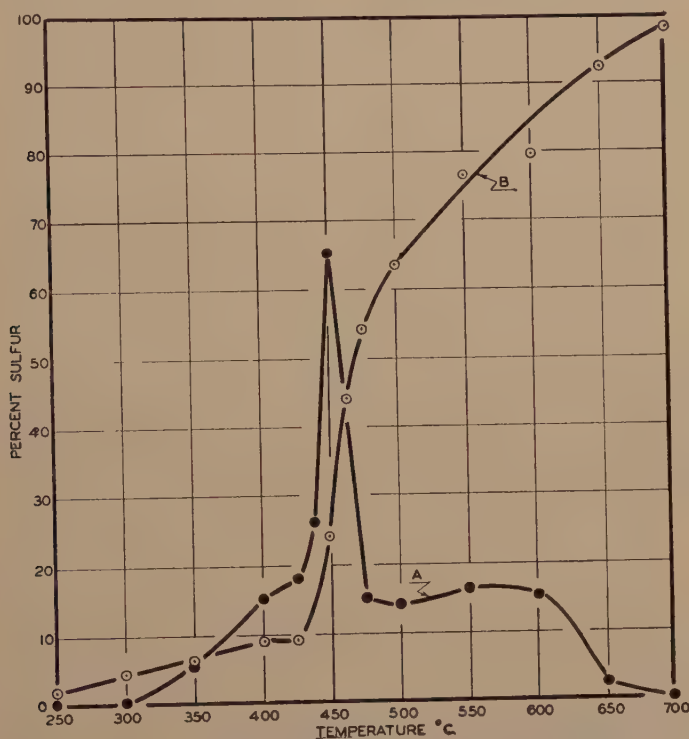


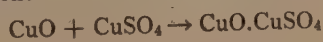
FIG 5—OXIDATION OF CHALCOCITE IN AIR AT VARIOUS TEMPERATURES.
A. Water-soluble sulphur (calculated from water-soluble copper)
B. Sulphur dioxide

and that, at 700°C, 98.26 pct of the sulphur in the sample of chalcocite has been removed as sulphur dioxide gas. Curve A for water-soluble sulphur was calculated from the water-soluble copper which is assumed to be copper sulfate. Therefore it follows the water-soluble copper curve, reaching its maximum at 450°C.

The removal of sulphur was studied more closely in the tests with oxygen, because it was found that at 700°C only about $\frac{3}{4}$ of the sulphur had been gasified, (curve B, Fig 6).

Sulphur analyses on the water-soluble products curve A, Fig 6, showed that the percentage of water-soluble sulphur indi-

cated the presence of cupric sulphate, was present in an acid-soluble form, probably basic cupric sulphate, $\text{CuO} \cdot \text{CuSO}_4$. This was identified by its physical appearance and insolubility in water. It resembled a sample of basic sulphate which we prepared and analyzed. It will be observed from curve C Fig 6 that the formation of basic sulphate commences at a little over 300°C. In the presence of cupric oxide, the temperature of formation of the basic sulphate is probably much lower than that of the transformation of normal sulphate into basic sulphate, because of the reaction:



This is confirmed by Sille⁸ who heated cupric sulphate and cupric oxide in the proportion 1:1 in a nitrogen atmosphere and observed the formation of basic sulphate

the calcine, however, red cuprous oxide (Cu_2O) was predominant in the "fusion zone" (from 400 to 550°C in tests with oxygen), while above 550°C most of the

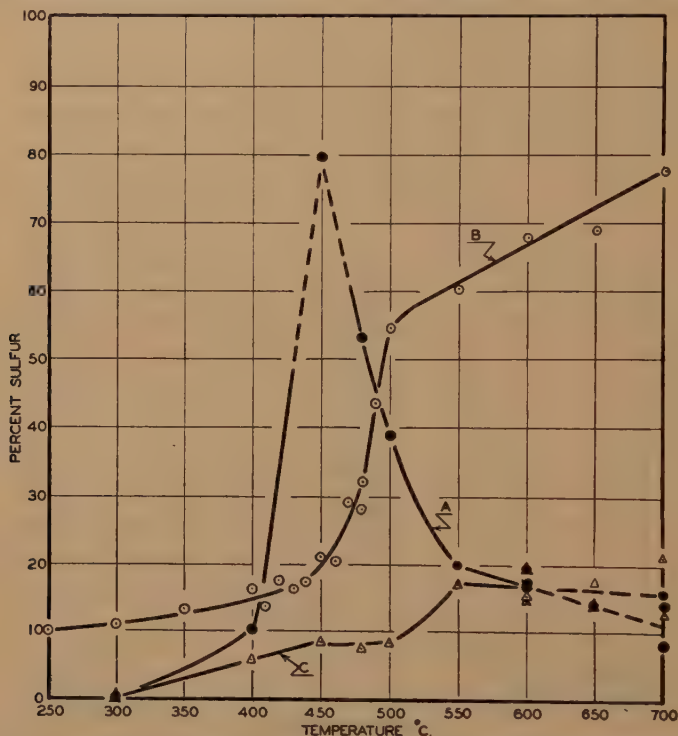


FIG 6—OXIDATION OF CHALCOCITE IN OXYGEN AT VARIOUS TEMPERATURES.

- A. Water-soluble sulphur
- B. Sulphur dioxide
- C. Acid-soluble sulphur

as low as 350°C. At 500°C, basic cupric sulphate increases at the expense of normal sulphate, and thus we have reciprocal curves between 500 and 700°C.

The importance of basic cupric sulphate in any reactions which occur during the oxidation of chalcocite in oxygen can be seen when it is realized that the weight ratio of sulphur to copper in $\text{CuO} \cdot \text{CuSO}_4$ is 1:4. Thus, at 550°C, 17.5 pct of the acid-soluble copper is basic sulphate, while the remainder is cuprous and/or cupric oxide. Simple analytical methods will not distinguish between cuprous and cupric oxides in a mixture of the two. From observation of

oxides appeared to be black cupric oxide (CuO).

The Fusion

One of the interesting results of this study was the observation that fusion and, in some cases fusion with "boiling," occurred in the neighborhood of 450°C. This could not be due to the fusion of chalcocite since its melting point is 1130°C. Fusion occurred in both the air and the oxygen oxidation of chalcocite. For the air oxidation, fusion did not occur below 450 nor above 460°C. On the other hand, using oxygen as the oxidant, fusion began as low

as 400°C and was observed as high as 550°C. From what has been stated above and from the curves *B* in Fig 3 and 4, it is apparent that the highest yields of water-soluble copper are obtained under those conditions where fusion occurs.

In some tests using air as oxidant, runs were made using natural chalcocite in place of that prepared in the laboratory. In these runs, the curves obtained were similar to those obtained with synthetic chalcocite, except that the yield of water-soluble copper was much lower. Thus at 450°C only 17.64 pct of the chalcocite copper was soluble in water as compared with 32.27 pct for the artificial chalcocite. In another series of runs, impurities such as pyrite, ferric oxide, silica, and ferrous sulphate were added to the synthetic chalcocite with results much like those obtained with the natural chalcocite. These results suggested that the impurities present in the natural chalcocite were responsible for the results obtained.

In this paper the authors have not presented the reaction mechanisms whereby chalcocite is converted through oxidation into other substances. However, we have done considerable work on this phase of the study, particularly investigating the reactions which cause fusion, and it is our intention to present our findings in another paper.

The data presented here show that chalcocite is converted into water-soluble copper (CuSO_4), water-soluble sulphur (CuSO_4), acid-soluble copper (CuO , Cu_2O , and $\text{CuO}\cdot\text{CuSO}_4$), acid-soluble sulphur ($\text{CuO}\cdot\text{CuSO}_4$) and a gaseous sulphur compound (SO_2). No doubt some sulphur trioxide (SO_3) is formed also but most of it is probably used up in forming copper sulphate or basic copper sulphate.

SUMMARY AND CONCLUSIONS

1. An apparatus is described suitable for studying the oxidation of chalcocite and other metallic sulphides.

2. A simple method of preparing a good quality synthetic chalcocite is described.

3. The effect of temperature on the oxidation of chalcocite, using air and commercial oxygen as the oxidants is presented in tables and in figures.

4. The optimum temperature for the oxidation of chalcocite to give water-soluble copper is in the neighborhood of 450°C.

5. The best yields of water-soluble copper are obtained when conditions are right for fusion to take place.

6. Commercial oxygen is a more effective oxidizing agent than air for the conversion of chalcocite into water-soluble substances.

7. Using commercial oxygen, an appreciable amount of basic copper sulphate is formed in the range 350–700°C. Probably basic copper sulphate is formed when air is the oxidant. However it was not determined analytically in these tests.

ACKNOWLEDGMENTS

The authors are indebted to Prof. J. W. Johns, Jr. for his interest and help in this work. We also wish to thank the other members of the metallurgy department for valuable suggestions and help.

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Vacuum Dezincing in Lead Refining

By W. T. ISBELL,* MEMBER AIME

(New York Meeting, March 1947)

IN the Parkes process of lead refining, after desilverization has been completed by means of the addition of zinc, there remains in the lead from 0.5 to 0.6 pct zinc. At this stage in the refining operations virtually all impurities are reduced to refined lead specifications except zinc and antimony. All excess copper, nickel and cobalt have been removed by the zinc additions. The silver remaining should not exceed 0.1 oz per ton. It then remains only to remove the zinc and antimony in order to produce refined lead.

At the Herculanum plant of the St. Joseph Lead Co., practice formerly was to complete the refining by means of oxidation in a reverberatory furnace. This process consisted of heating the lead to 1400° to 1500°F and allowing it to come in contact with excess air passing over the surface of the lead and periodically agitating the bath of lead with air. This procedure not only resulted in the loss of zinc but of a considerable quantity of lead converted to the oxide in the form of dross and fume. The fume, collected in the baghouse, together with the dross was returned to the blast furnace, thus adding appreciably to the circulating load on the blast furnace and refinery. In addition, operation and maintenance of the reverberatory furnace were expensive and required the performance of disagreeably hot and somewhat hazardous work.

The process of dezincing with high

vacuum was developed at this plant as a substitute for the oxidation process and finally led to lower operating costs, the practical elimination of dross and fume and the direct production of metallic zinc, which is very suitable for re-use in the desilverization process.

Essentially this process consists of subjecting the lead to high vacuum, in a kettle provided with means for heating, a bell-shaped member open at the lower end so constructed that it can be immersed in the molten lead, and means for evacuating the interior of the bell and for sealing an agitator. Metallic zinc is thus produced and collects on the upper cooled part of the bell member. This metallic zinc is periodically removed and re-used in the desilverization process.

The process is quite simple. It is conducted at a low temperature, thus permitting the use of iron equipment, and shows a material saving in refining costs over the old method.

EQUIPMENT AND ITS USES

Dezincing Machine.—The equipment employed in this process consists of a dezincing machine, a steel kettle of 120 tons capacity, a vacuum system and equipment for handling the dezincing machine (Fig 1). The dezincing machine consists of a compact assembly, suitable for handling with an overhead crane, consisting of a treating chamber and the agitating mechanism.

Treating Chamber.—The treating chamber is a bell-shaped shell (4), similar in shape to a hemispherical kettle with a lid

Manuscript received at the office of the Institute Dec. 2, 1946. Issued as TP 2138 in METALS TECHNOLOGY, April 1947.

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welded on and its bottom cut out. The shell is 10½ ft in diameter at the top and 64 in. high. It is formed and welded from 1-in. firebox-steel plate. A cylindrical water jacket (5), 6 in. high, covers the entire top of the shell. Cooling water enters this jacket at two diametrically opposite points and flows from an outlet at the top of the exhaust jacket (15). Heavy I-beams, welded to the top of the bell-shaped shell, with their ends welded to an encircling ring of heavy channel iron, make up the condenser frame (3). To this heavy frame are welded several supporting brackets (10), with adjustable studs (12), and these carry the weight of the machine.

Agitating Mechanism.—Agitation is obtained by a 22-in. four-bladed impeller (7), turning inside a cylindrical shroud. The impeller shaft tube (23), in which the impeller shaft turns, extends from just above the top of the impeller hub and through the top of the chamber and water jacket. This tube being carefully welded into the top of the chamber and water jacket, and being of sufficient length to extend into the molten lead to a depth greater than the height of a column of molten lead, equal to atmospheric pressure, provides a liquid seal around the shaft. A pipe shield (21) is used to protect the impeller shaft tube (23), as there is some slight corrosion by zinc at the surface of the molten lead. A 15-hp motor, equipped with V-belt drive, rotates the impeller shaft, with suitable reduction gears, at a speed of 165 rpm.

Vacuum System.—Evacuation of the treating chamber is obtained by means of a Kinney D.V.D. 14 by 14-in. vacuum pump (17), equipped with an oil separator (18), and relief valve (22), and connected to the treating chamber by means of an 8-in. vacuum line (6), having a swing joint and a flexible rubber expansion joint (11). The pump is driven by means

of a 25 hp. motor (20) equipped with V-belt drive.

OPERATION OF PROCESS

As soon as the desilverizing step in the lead refining cycle is completed, the charge of 110 to 115 tons of desilverized lead, containing 0.5 to 0.6 pct zinc, is pumped into the 120-ton dezincing kettle. The lead is heated to 750° to 800°F, then skimmed free of froth and dross. The vacuum dezincing machine is then set in place. Water connections to the cooling jacket are made immediately and sufficient water is turned on to prevent formation of steam in the jacket. The studs on the support brackets are adjusted to such a height that a molten lead seal is maintained between the outside and inside of the treating chamber during operation. In this adjustment, once made, change is necessary only when the lead tonnage varies more than 10 tons, which is very seldom.

When the machine is set in place, the temperature drops 30° to 50°F, and while the temperature is being brought up the connection is made to the vacuum line. When the temperature has risen to 1080° to 1090°F, the bleeder valve in the vacuum line near the pump is closed and the vacuum pump is started. When the pressure has dropped to 0.5 mm Hg the agitator is started. The temperature is brought up to 1100°F and held as near as possible to that degree for the duration of the "treating time," which at present is 5 hours.

At the expiration of the 5-hr "treating time" the fire on the kettle is cut off, the agitator is stopped, the pump is shut down and the bleeder valve in the vacuum line is opened, to allow the pressure in the treating chamber to rise to atmospheric. The vacuum line is then disconnected and swung upward out of the way of the crane and the water lines are disconnected. The dezincing machine is then lifted out of the kettle by means of an overhead

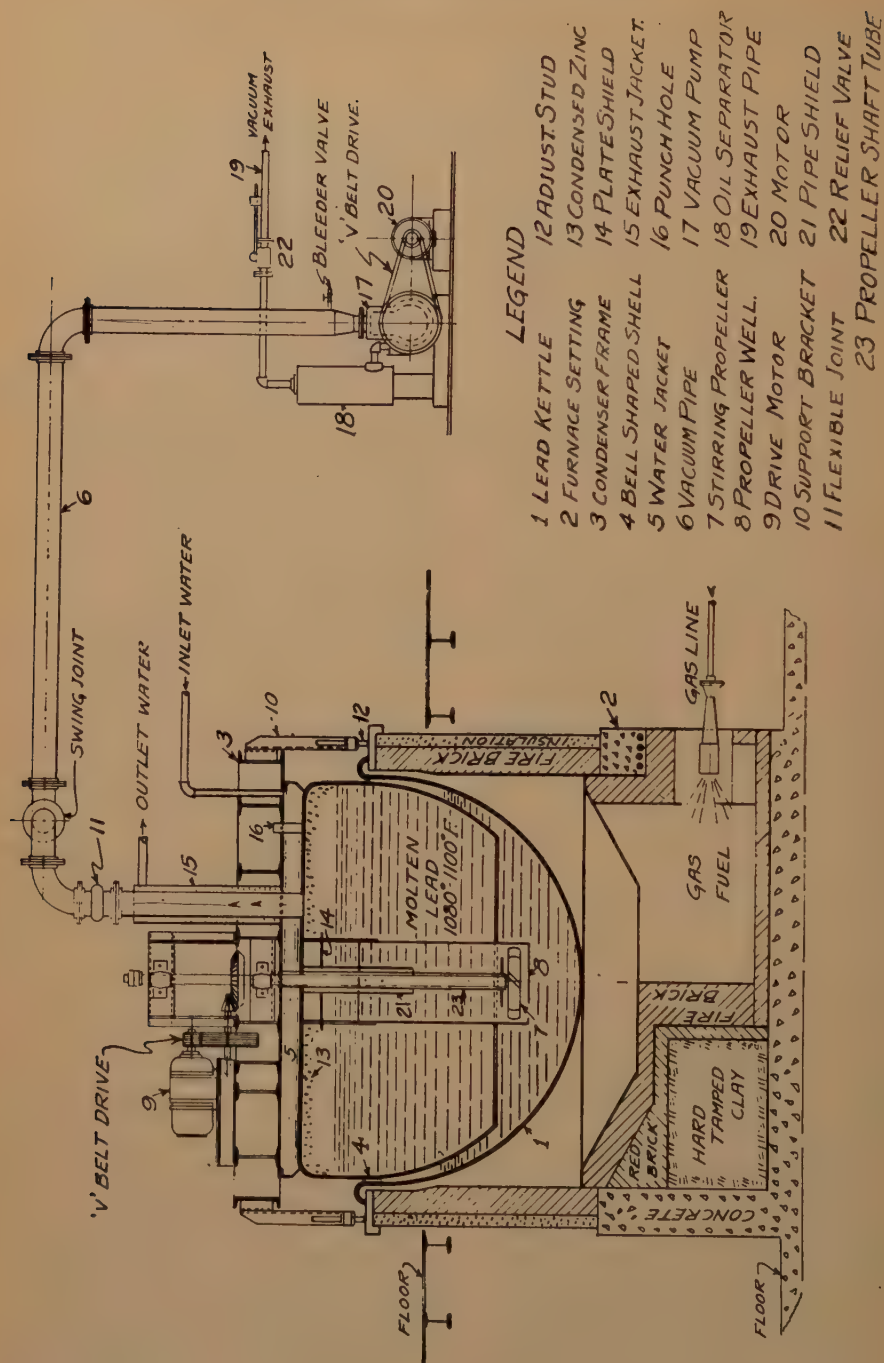


FIG 1—DEZINCING MACHINE.

crane and set on three steel A-frames, either to cool for the removal of the zinc or to await its use on the next charge of desilverized lead. The zinc condenses in a coherent, crystalline mass, loosely attached to the underside of the water-cooled top of the treating chamber.

The condensed zinc is removed after two or three charges of desilverized lead have been treated, depending on the convenience of the operator. The bulk of the zinc is removed by vibrating the steel head, to which the zinc is attached, with a lightly held air hammer, fitted with a short bar having a flat bronze head. This bar is inserted through capped holes in the top of the water jacket. Any deposit not shaken down by vibration is removed from the inside of the treating chamber after the latter has cooled sufficiently for a man to work in it, with a light chipping hammer and hand bars.

The metal condensate from each cleaning is held separately on trucks until it is evaluated by assays and tonnage of lead treated, then it is re-used in the desilverizing kettles. The condensed metal contains a variable quantity of lead, and in order to arrive at a zinc value on which to base its use for desilverizing purposes samples are taken just before the dezincing machine is set in place and just after it is taken out of the dezincing kettle. These samples are assayed for zinc content. Their differences and the estimated weight of lead treated serve as a basis for calculating the quantity of zinc recovered from each charge of desilverized lead treated. The sum of these quantities deposited from individual charges between cleanings is assumed to be the total zinc content of the condensates removed on cleaning. Values thus obtained have served very satisfactorily as a basis for the use of the recovered zinc in desilverizing.

Throughout the dezincing process, temperatures are recorded automatically. Pressure readings are taken at frequent

intervals and are recorded each hour. In $1\frac{1}{2}$ to 2 hr the pressure normally drops to 0.05 mm Hg, and remains there to the end of the treatment. If the pressure does not drop normally, the operator looks for the cause—usually a leaky joint; less often, emulsified oil in the vacuum pump. Sometimes the trouble is caused by a crack in the chamber wall or by poor lead seal around the bottom of the chamber or around the impeller shaft. A leaky joint or crack in the chamber wall is indicated by continued unsatisfactory high pressure and exhaust from the pump. A leaky joint usually requires the tightening of the flanges or replacement of the rubber gaskets. A crack in the chamber wall or around the impeller shaft is repaired by welding. When oil becomes emulsified it must be replaced by new oil.

METALLURGY

The vacuum dezincing process at the Herculeum plant has recovered well over 90 pct of the zinc content left in the lead after desilverization and almost all the cadmium. Very little antimony is removed in this process; this metal must be removed by any of the well-known processes prior to desilverization or after the dezincing.

ACKNOWLEDGMENTS

The present successful commercial application of this process represents in a large measure the painstaking and loyal assistance of my associates. I wish to acknowledge this service on the part of Mr. C. H. Briggs, in the design of the equipment, and Mr. Finis Huddleston, who contributed no small part to the present successful operation of the process.

DISCUSSION

(*W. E. Milligan and T. D. Jones presiding*)

A. BUTTS*—Approximately how much lead is carried over with the zinc?

* Bethlehem, Pa.

W. T. ISBELL (author's reply)—Varying amounts of lead are carried over depending on agitation and splashing. Estimate 2-10 pct.

A. J. PHILLIPS*—Have you encountered any elements or impurities in the lead which interfere in any way with the vacuum dezincing process?

W. T. ISBELL—We have not.

A. BUTTS—The operating conditions stated by the author for this interesting and ingenious application of vacuum metallurgy to the dezincing of lead afford the basis for calculations which suggest that considerable benefit might be realized by a relatively small increase in operating temperature, say from 1100 to 1200°F. There are obvious advantages in using a low operating temperature, and these may have figured prominently in the development of the process at Herculaneum. The author has probably tried different temperatures, pressures, and times. Nevertheless, the difficulties involved in variation of the conditions in large-scale operation may have limited such experimentation, so that theoretical calculations may be useful, as well as of interest for comparison with the results actually obtained.

The controlling factors given, in addition to the temperature of 1100°F, are the operating pressure of 0.05 mm and a "recovery of well over 90 pct of the zinc content left in the lead after desilverization, the treating time for these conditions being 5 hr. Presumably the stated recovery of zinc means that the zinc content of the desilverized lead is reduced by the treatment from about 0.55 pct to something less than 0.05 pct. These weight percentages correspond to approximately 1.7 and 0.16 at. pct, respectively. The vapor pressure of pure zinc, obtained by means of the formula

$$\log p = - \frac{6789}{T} - 1.051 \log T - 0.0001255T + 12.018$$

(where T is the temperature in degrees Kelvin and p is the vapor pressure in millimeters of mercury), is 9.60 mm at 1100°F and 26.5 mm at 1200°F. The vapor pressure of the zinc in solution in the lead is thus $0.017 \times 9.60 = 0.163$ mm at the start of the distillation. Since this pressure is above the opposing pressure of 0.05 mm, zinc will actively "boil" from the alloy, but the rate of its evaporation will become much slower as the remaining zinc content drops to a percentage which will bring its vapor pressure below 0.05 mm. This percentage is about 0.16 pct by weight. Calculations indicate that when the percentage has fallen to 0.05 by weight, the zinc is evaporating at a rate comparable with evaporation of water at about 160°F under normal atmospheric pressure.

At 1200°F the vapor pressure of the zinc in solution in the lead would be $0.017 \times 26.5 = 0.45$ mm at the start of the distillation and about 0.042 mm when the zinc content had fallen to 0.05 pct, which is only slightly below the opposing pressure. The required time should then be reducible to much less than 5 hr. If the time were to remain at 5 hr, the zinc content of the lead would become less than the percentage now obtained, but it does not appear that the gain on this score would justify the higher temperature, while the possible saving in time might well do so.

The calculated vapor pressures of the lead and of the antimony at 1100°F are very small. It is indicated that the lead content of the distillate should be under 0.1 pct and its antimony content even less. Their contents would be raised slightly at 1200°F, but it is readily shown that the amount of the increase would be too small to be of practical importance in the process.

* American Smelting and Refining Co.

Soda Treatment of Blast-furnace Drosses at El Paso Smelter

By A. A. COLLINS,* MEMBER AIME

(New York Meeting, March 1947)

OF widespread interest to all lead metallurgists is a dross smelting process that will consistently give mattes and speiss of low lead and high copper contents. It is a problem that has intrigued operators through the years. In the past few years, with increased amounts of copper and overcrowded metallurgical furnaces, it has been almost imperative to evolve some method. Experience at El Paso has shown that high copper-to-lead ratios can be consistently attained by use of the new soda process.†

OLDER METHODS

Three older methods, i.e.,

1. Dross plus siliceous ore and limestone,
2. Dross plus one fourth blast-furnace speiss and siliceous ore,
3. Dross plus sulphides and siliceous ore and scrap iron,

do not give consistent results and the products are higher in lead and lower in copper than those produced with the soda process. Any radical changes in the blast-furnace drosses will throw any of these older methods into a tailspin.

For almost ten years, El Paso used the third method, with varying results. It was noted that as the arsenic and anti-

mony contents of the dross increased, the speiss and matte steadily increased in lead and decreased in copper.

A dross containing four parts of copper to one part of arsenic was considered to be ideal. At times this balance of copper to arsenic was almost impossible to obtain, especially when handling copper Cottrell dusts, which vary so greatly in copper and arsenic. Custom smelters like El Paso, handling a great variety of dusts, concentrates and ores, are apt to have anywhere from 1 to 15 pct copper on charge, with a variable in arsenic of from 0.5 to 2 pct.

With such conditions, and drosses varying from 12 to 40 pct copper, an operator using the older dross reverberatory practices would find it just about impossible to control the reverberatory operations and to produce a good product low in lead and high in copper. These conditions prevailed at El Paso from the year 1940 to the present. In May 1942 it was decided to experiment with the soda process.

THE SODA PROCESS

After considerable work the soda method was finally evolved to the present state. It has never failed to produce a good product even under the most adverse conditions. It might be well to remember that many men of thought in the smelting industry have at one time or other suggested the removal of all copper, arsenic and antimony from the lead blast-furnace charge as an aid to better metallurgy.

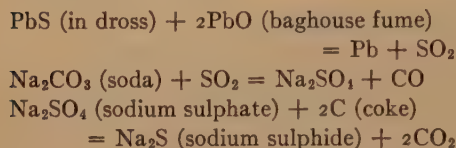
Manuscript received at the office of the Institute Nov. 9, 1946. Issued as TP 2139 in METALS TECHNOLOGY, February 1947.

* General Superintendent, Chihuahua Plant, American Smelting and Refining Co., Chihuahua, Chih., Mexico.

† Developed under the direction of Edward P. Fleming, Consulting Metallurgist, American Smelting and Refining Co., the process is covered by the following U. S. Letters Patent: E. P. Fleming and Donald H. McIntosh, Nos. 2343760 and 2343761; Arthur A. Collins, No. 2381970.

These three elements need not be segregated with the use of soda.

The four reagents used in the soda process are: (1) soda (Na_2CO_3), (2) litharge or baghouse fume (PbO), (3) coke, (4) sulphur (S). The reactions are:



The soda sulphide (Na_2S) matte acts as a collector for all of the iron as contained in the dross and, since no silica, sulphide or limestone is added, no slag is produced. Hence, with no iron silicates to form, less heat as British thermal units is required in the furnace, which gives a cooler furnace with a better separation of the lead and speiss. The two older methods (dross plus siliceous ore and limestone, and dross plus sulphides, siliceous ore and scrap iron) require considerably more heat to prevent the formation of magnetite, which causes a poor settling furnace and a high lead in the resultant matte and speiss.

The sulphur is added when not enough sulphur is available in the dross to form sufficient sodium sulphide (Na_2S) to hold the magnetite in solution. In such cases sufficient sulphur is added to the charge along with the sodium carbonate and litharge flux to be available to form sufficient Na_2S to maintain substantially all of the iron sulphide (FeS) in solution in the soda matte. The sulphur addition serves two purposes: (1) the formation of Na_2S and (2) the conversion of all Fe to FeS , the sulphur tending to keep a dross reverberatory in excellent condition and free of magnetite accretions.

OPERATION OF PROCESS

There are no lead wells on the El Paso blast furnaces; all lead is tapped from the furnace with slag into a large settler, where the lead settles out and slag passes through

an additional settler before entering the slag pot. In the soda process, the molten blast-furnace lead is transferred from the settler into a brick-lined pot suspended on a carriage; the latter is hauled by an electric locomotive and the molten lead is dumped into one of three 65-ton receiving kettles (Fig 1). When sufficient lead has been placed in one of these kettles, a stirrer or mixing machine is placed in the kettle, to dry the dross and to mix the soda ash, which has been already added. The amount of soda ash added to each kettle is somewhere between 3 and 5 pct of the dross tonnage, dependent upon the amount of dross and its iron and zinc content. The receiving kettle is stirred continuously until filled, when the stirrer is removed and the drossing begins. The dross is fairly dry, and the soda ash is well mixed with it. An average of 25,000 lb of dross per kettle is produced with 1000 lb of soda consumed.

The dross is removed from the surface of the lead by an Owens grab bucket attached to a crane (Fig 2). Grabs of 3000 to 6000 lb of dross are made, the lead is drained out and while the lead is draining a mixture of one part sulphur, one part Dwight and Lloyd baghouse dust and one part coke breeze is added to the top of the dross in the grab bucket, to the extent of 1 to 3 pct of the dross weight. The dross is now dropped into the dross reverberatory, where it is smelted, using 3,000,000 to 4,000,000 Btu of heat per ton of dross. This dross is charged at intervals, but never is a mound allowed to form by too fast a charging rate. A charge is always smelted out before another is added. The charging practice (Fig 3) is similar to that of the large copper reverberatory at El Paso, where charging is done at intervals, but never with a mound, and when a charge is smelted another one is introduced.

Whenever we have a full furnace on an average bath of 45 in., we remove all of the soda matte before tapping any lead; for

in any matte left in the furnace some of the iron is likely to revert to magnetite, which will settle out in the furnace and cause accretions. The lead is now tapped out,

opened and the upper layer of speiss removed, about 9 in. This upper layer is very low in lead, about 6 pct, and high in copper, about 67 pct. The layer of speiss

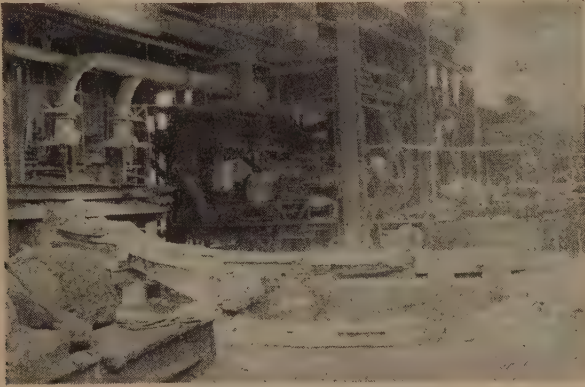


FIG 1—DROSSING KETTLE.

down to speiss. This still leaves some 12 in. of lead on the bottom of the furnace, which will protect the bottom and aid in cooling the total bath of lead. The average copper in the lead removed is 0.20 pct, whereas with no bath of lead remaining

directly above the lead is high in lead, about 20 pct, and lower in copper, about 60 pct. The diagram in Fig 4 will help to explain the tapping cycle of the dross reverberatory.

Thus when the tapping cycle is complete

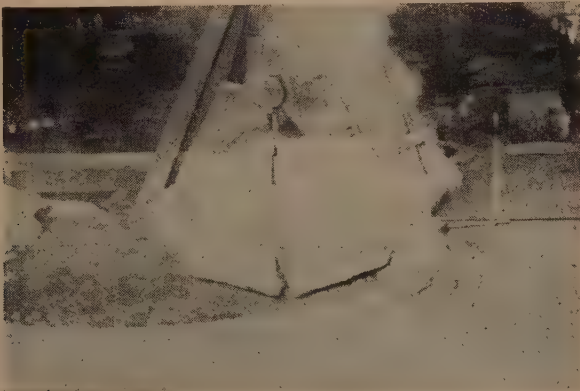


FIG 2—GRAB BUCKET DROSSING RECEIVING KETTLE.

in the furnace and the lead taphole on the bottom of the furnace, this lead is very apt to contain up to one per cent copper. As mentioned, the lead is removed down to speiss; this leaves about 28 in. of speiss in the furnace. The speiss hole is now

there is left in the furnace before recharging: lead, 12 in.; speiss, 19 in.; total, 31 in. The bottom layer of the speiss is very impure (high in lead).

The positions of the tapholes, lead, speiss and matte skim on a horizontal

plane with relation to the forced-draft burners are as important as the vertical heights.

the burners toward the uptake or exit end of the furnace, for the complete removal of matte. The natural movement of the

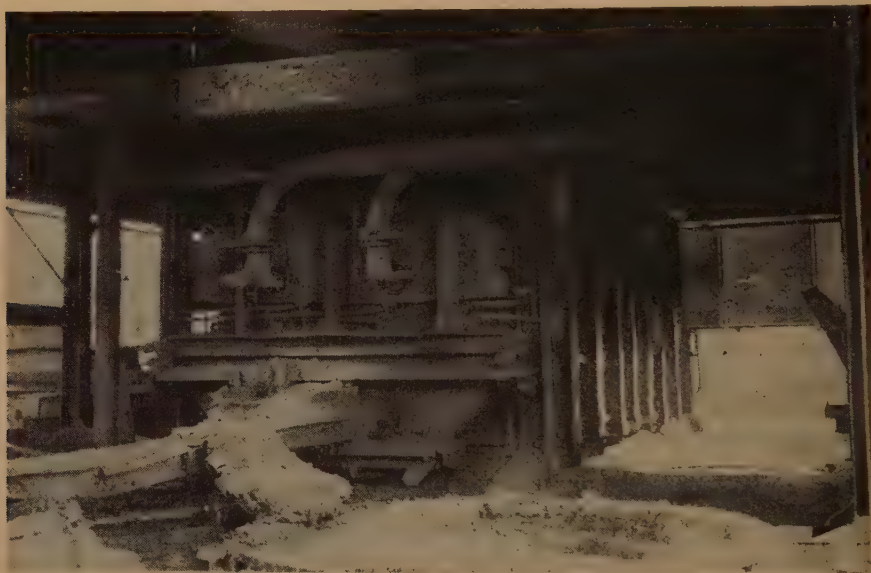


FIG 3—GRAB BUCKET CHARGING DROSS REVERBERATORY.

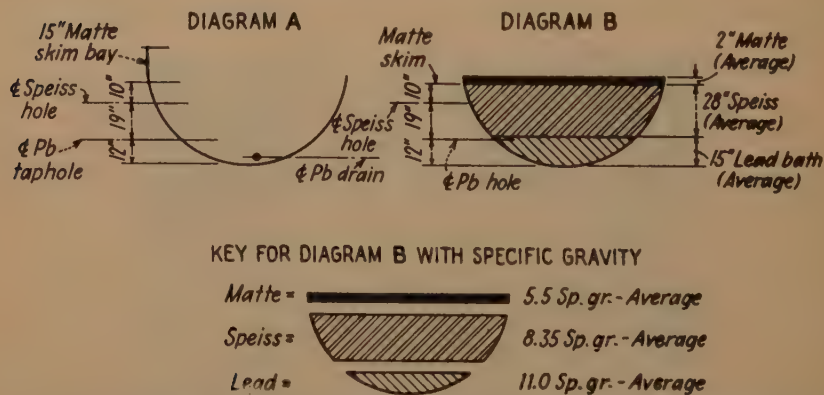


FIG 4—CROSS SECTION OF DROSS REVERBERATORY FURNACE CRUCIBLE.

Step 1. 2 inches matte removed by skimming high hole in 15-in. matte skim bay. Diagram B.

Step 2. 3 inches lead tapped through "Pb hole" until a little speiss shows. Diagram B.

Step 3. 9 inches speiss tapped through "speiss hole." Diagram B.

The speiss taphole should be in the cool part of the furnace about two thirds the furnace distance from the burners, for a good clean speiss. The matte skim bay should be three fourths the distance from

furnace is toward the exit end away from the burners.

SUMMARY

1. The soda process is in successful use at four other plants of the American

Smelting and Refining Co., namely, Chihuahua, Selby, Murray and Helena. Murray and Selby are smelting high antimonial drosses and Chihuahua high arsenical. Thus with El Paso handling high-copper drosses, the soda method can handle drosses high in copper, arsenic and anti-

the cooler temperature at which the furnace is operated. Also, no slag is produced as formerly, which contained approximately 2.5 pct copper and was resmelted in a lead blast furnace. Between this and the low copper content of reverberatory lead bullion a run-around of about 15 pct has

TABLE 1—Comparison of Products

Year	Time	Analysis of Speiss and Matte, Pct							Ratio Cu:Pb
		Au	Ag	Pb	Cu	As	Sb	Ni	
1940	Before soda	1.62	48.1	19.9	40.41	8.62	2.83	0.08	2.0:1
1941	Before soda	1.77	24.1	17.7	39.62	8.42	1.89	0.10	2.2:1
1943	After soda	0.93	29.7	8.5	57.26	7.22	1.43	0.09	6.7:1
1944	After soda	0.83	27.6	9.1	52.53	6.58	1.15	0.10	5.8:1

Complete Analysis of Separated Products, Using Soda

Date	Product	Au	Ag	Pb	Cu	SiO ₂	Fe	CaO	Zn	S	As	Sb	Ni
Aug. 1943	Speiss	2.33	49.9	4.4	72.35	0.8	0.2	0.1	...	0.1	19.20	2.30	0.08
	Matte	0.15	15.0	6.3	42.80	5.8	7.5	0.1	3.0	14.2	1.03	0.35	0.01

Analysis of Drosses, Pct

Year	Pb	Cu	As	Sb	Ratio Cu:As + Sb
1940	53.96	29.52	5.80	3.39	3.2:1
1941	54.30	29.50	6.69	1.76	3.5:1
1943	55.90	29.10	4.90	1.30	4.7:1
1944	61.90	20.40	4.30	1.00	3.8:1

TABLE 2—Data for Years 1943 and 1944

Year	Dross Analysis, Pct				Analysis of Speiss, Pct							Analysis of Matte						
	Pb	Cu	As	Sb	Au	Ag	Pb	Cu	As	Sb	Ni	Au	Ag	Pb	Cu	As	Sb	Ni
1943	55.9	29.1	4.9	1.3	1.88	47.9	8.1	68.84	15.29	2.35	0.20	0.27	17.0	8.8	49.17	1.57	0.78	0.02
1944	61.9	20.4	4.3	1.0	1.87	48.3	8.5	68.31	14.99	2.12	0.22	0.28	16.7	9.3	44.29	2.19	0.65	0.03

mony under all sorts of conditions (Tables 1 and 2.)

2. There is no need for concentrators to drop copper and arsenic, as suggested by Dice, Oldright and Brighton.¹

3. Dross reverberatories can handle more tonnage using the soda process, as there is less recirculation of copper because reverberatory lead has only 0.2 pct copper, against 2 pct in the older methods, and

been eliminated. Such a run-around entails an appreciable metal loss of copper, lead and silver.

4. According to Gerald U. Greene,² pure Cu₃As (the eutectic) will contain: Pb, 6.38 pct; Cu, 76.80; As, 16.81.

El Paso has successfully produced speiss of: Pb, 4.4 pct; Cu, 72.35; As, 19.20; Sb, 2.30, (which is less than the eutectic in lead.)

¹ Dice, Oldright and Brighton: *Trans. A.I.M.E.* (1937) 121, 127.

² G. U. Greene: *Trans. A.I.M.E.* (1937) 121, 171.

5. Antimony has always caused excessive lead carry in dross-furnace products when the older methods were used (El Paso February 1940 speiss shows): Pb, 19.6; Cu, 32.5; As, 6.10; Sb, 8.20.

With soda, our Murray plant shows, with 16.9 pct Sb in speiss, only 10.6 pct Pb and 58.4 pct Cu.

6. The soda process produces a high-grade product in one step, whereas formerly two steps were necessary; i.e., speiss was tapped from the reverberatory and poured into another small furnace, where air and heat were applied.

7. Soda matte is rather hard on brick-work, therefore El Paso and Chihuahua are using water-jacketed side walls at matte line, with low maintenance expense.

8. Granulated soda speiss can be successfully roasted for arsenic without finer grinding.

9. The soda method is easier on the reverberatory arch than older methods, because of the lower heat required. El Paso, using a 12-in., 70 pct alumina brick in arch, has obtained an arch life of 15 months, which surpasses any previous campaign at El Paso.

10. Before the use of soda ash, the long El Paso reverberatory, 27 ft 7 in. by 8 ft 4 in., was troubled with magnetite accretions, which could be only partially removed with scrap iron and sulphides. With soda the furnace is free of magnetite at all times.

11. Less oxygen is required for opening tapholes with the soda process, as the furnace is always in good shape.

12. Metal losses are less in tapping soda speiss and matte, as the temperatures are lower than with the other methods. There is no lead fume while tapping lead, whereas previously there was considerable trouble with fume.

13. Magnetite can be removed by soda at a much lower temperature than when silica and scrap iron are employed as fluxes. At lower temperatures the solu-

bility of lead in copper arsenide and copper antimonide is naturally reduced. The compound copper arsenide accounts for approximately 75 pct of speiss composition. At the freezing point of this compound, which is approximately 650°C, it contains about 6 pct lead in solution. At 1000°C., it contains about 16 pct lead in solution. The furnace can operate in a satisfactory manner with speiss at a temperature of about 700°C., which will carry 4 to 10 pct lead. It is advantageous to operate at a low temperature. The production of silicate slag does not permit low-temperature operation.

14. Lower temperatures for operating the soda process have several additional advantages. There is less fuel consumption and the lead produced contains less copper than with the previous method of operation. With the new process the lead contains about 0.2 pct copper, while formerly it carried between 2 and 3 pct copper, the latter entailing a considerable run-around of copper that had to be handled and resmelted as dross.

15. Chemical and microscopic examination of the speiss produced shows that we are nearing a true mixture of copper arsenide and copper antimonide, with a minimum of lead in solution and scarcely any in suspension.

16. Leady copper mattes with high lead and low iron content can be treated successfully with the soda flux in the dross reverberatory and much of the lead can be recovered as metallic lead. At El Paso, matte containing 30 pct Pb and 40 pct Cu with 8 pct Fe has been processed to produce a matte of 8 pct Pb and 40 pct Cu.

DISCUSSION

(W. E. Milligan and T. D. Jones presiding)

W. T. ISBELL*—We have tried out the soda treatment of our blast furnace drosses on a

* Herculaneum Smelter, St. Joseph Lead Co.

laboratory scale and so far we have not had very much success with this method. Do you know what effect the nickel and cobalt might have on this method in regard to obtaining a high ratio of copper to lead in the matte? All of our experimental tests on our drosses by the soda treatment result in very little improvement in the copper-lead ratio in our matte. The absence of arsenic and antimony in our drosses in combination with presence of nickel cobalt may be the answer. I would like to know if Mr. Collins has an answer to this.

At our Herculanum Smelter we produce lead-copper matte on blast furnace and we have always had great difficulty in producing

a matte with a much greater ratio of 1 to 1 copper to lead. We have always considered the cause of this to be the presence of nickel and cobalt and the absence of arsenic and antimony.

A. A. COLLINS (author's reply)—Without seeing an analysis of the Herculanum drosses my belief is that since he has no arsenic or antimony he is short of collector for his copper, nickel and cobalt and to matte out these metals successfully he will require the addition of sulphur in the form of either a sulphide ore, such as pyrite, or native sulphur. Naturally, utilizing the soda process native sulphur is preferable.

Distillation of Zinc and Refining of Residual Metals from Copper-base Alloys

BY FRANK F. POLAND*

(Chicago Meeting, February 1946)

THE purpose of this paper is to describe a new process for the refining of secondary copper-base metals and a specially designed high-temperature electric-resistor furnace used in the process for the distillation of zinc from these metals.

The process was used for the conversion of nickel silver to cupronickel and to recover the zinc content in metallic form. It also proved applicable and economical for the treatment of scrap brass for separating and reclaiming the copper and zinc.

The relatively large furnace developed for the distillation of zinc is described in detail, for it made economically possible the direct recovery of metallic zinc from scrap brass, which is a new step in the processing of such material. Considerable interest has been shown in the utilization of the distillation furnace for other metallurgical processes, where it is of advantage to operate in a controlled neutral or reducing atmosphere, or to avoid having the processed metal in contact with refractories other than carbon, or to operate at temperatures between 3000 and 4000°F.

PURPOSE OF DEVELOPMENT

It was recognized early in the war effort that nickel would become a critical metal,

therefore all nickel stock and alloys containing relatively high percentages of nickel were frozen immediately. Among these alloys were considerable quantities of various grades of nickel silver, an alloy containing copper, nickel, zinc, and in some grades lead, also minor amounts of iron, manganese and other constituents.

At the time there was no existing plant or process to eliminate the zinc, lead, and minor constituents so as to convert this metal to cupronickel, one of the important alloys needed by the U. S. Navy for condenser parts. Therefore the Bureau of Industrial Conservation of the War Production Board requested the executives of the leading nonferrous metal companies to have their metallurgical staffs study the problem of converting this metal to cupronickel conforming to U. S. Navy Specification 44T40. The composition specified therein is as follows: nickel, 29 to 32 per cent; zinc, 1.00; iron, 0.00 to 0.60; lead, 0.05; tin, 1.20; manganese, 0.00 to 1.00; total of other elements (maximum), 0.50; copper, remainder.

The problem in converting these alloys to cupronickel was the elimination of zinc, lead, iron, manganese, and other elements without appreciable loss of nickel to slags or other by-products.

Revere Copper and Brass Incorporated, through its Research and Development Department, undertook to solve this problem. A Government-owned plant was built at Rome, N. Y., and there the conversion was made successfully.

Manuscript received at the office of the Institute Dec. 1, 1945. Issued as TP 2065 in METALS TECHNOLOGY, September 1946.

* Administrative Assistant to Vice President in Charge of Research and Development, Revere Copper and Brass Inc., Rome, New York.

TYPE AND ANALYSIS OF MATERIALS
TREATED

The major portion of the metal, approximately 6000 tons, processed in this plant consisted of nickel-silver alloys, the analysis varying between the following limits: nickel, 5.0 to 20.0 per cent; zinc, 15.0 to 30.0; lead, 0.01 to 2.5; iron, 0.05 to 0.5; manganese, 0.05 to 0.50; copper, balance. The zinc averaged approximately 20.0 per cent and the nickel 14.0 per cent.

Included in the nickel silver treated were 225 tons of discarded keys obtained through a national salvage collection. The analysis of this material after it had passed over a magnetic separator was typical of 2.5 per cent leaded nickel silver, except that the iron content was approximately 1.0 per cent and the tin 0.75 per cent, owing to the presence of iron and bronze keys.

The nickel silver received was classified into two grades—low lead, i.e., material containing not more than 0.05 per cent lead, and all material containing over 0.05 per cent lead. These were segregated as received and processed separately. It was a simple matter to make this segregation, for the metal received came mostly from stocks of known lead analysis.

Approximately 500 tons of refinery-grade scrap brass was also processed. The average meltdown analysis of this material was: copper, 72.0 per cent; zinc, 25.0; nickel, 0.2; iron, 0.35; lead, 1.0; tin, 0.75; silicon, 0.10; aluminum, 0.5, and manganese, 0.1.

A small amount of scrap Monel metal, 250 tons of fired cartridge cases and some copper containing approximately 15 per cent iron, were also processed. These items are not discussed in detail because they required only minor changes in the converter operations. However, they are mentioned to show the general adaptability of the process and equipment for the treatment of copper-base secondary metals.

RECOVERY AND ANALYSIS OF PRODUCTS
AND BY-PRODUCTS

The final cupronickel or copper was all cast into ingots. The cupronickel ingots were remelted with virgin metals in other plants, using up to 50 per cent by weight per furnace charge, to produce specification cupronickel. No difficulties were encountered in casting the mill shapes or in fabrication.

The copper ingots were used in the same manner and with the same good results for making brass mill products.

There was a direct recovery of 95.0 to 97.0 per cent of the copper plus nickel content of the nickel silver treated. The approximate 5.0 per cent loss went to the slags, which were shipped to an electrolytic copper refinery where practically all of the copper and a portion of the nickel as nickel sulphate were recovered.

The analysis of the cupronickel ingots obtained from the treatment of nickel-silver alloys was: nickel, 15.0 to 20.0 per cent; lead, 0.0 to 0.05 per cent; iron, 0.2 per cent, manganese, zinc, tin, silicon, aluminum each less than 0.002 per cent, copper, balance.

The direct recovery of copper from the treatment of refinery brass scrap was 95.0 per cent; the loss also went to slag, which was shipped to an electrolytic copper refinery, where a further high recovery was made.

The analysis of the copper ingots obtained from the treatment of refinery-grade scrap brass was: nickel, 0.25 per cent; iron, 0.002; lead, 0.01 to 0.05; tin, 0.002. Manganese, silicon, aluminum, and zinc were nil; arsenic, antimony, selenium, tellurium, and sulphur approximately the same as present in electrolytic copper.

An average of 85 per cent of the zinc contents of the nickel-silver alloys was recovered as slab zinc. The zinc recovery varied between 82.0 and 90.0 per cent, depending upon the amount of zinc on the

furnace charge; the raw material highest in zinc yielded the highest percentage recovery.

The analysis of the zinc from the nickel silver containing not more than 0.05 per cent lead was: lead, 0.04 to 0.10 per cent; nickel, 0.02; iron, less than 0.01 per cent; copper, 0.75.

The analysis of the zinc from the high-lead nickel silver was practically the same except that the lead content varied from 1.0 to 2.0 per cent, depending upon the amount of lead on the furnace charge.

In the treatment of the scrap brass and fired cartridge cases, the zinc recovery varied between 85.0 and 92.0 per cent, the recovery being the same as obtained from nickel silver containing the same percentage of zinc.

The analysis of the zinc from the scrap brass was practically the same as the zinc produced from high-lead nickel silver except that the nickel was less than 0.001 per cent.

All of the zinc recovered was used in making brass alloys; therefore the relatively high copper content, 0.75 per cent, did not detract from its usefulness or value.

The only by-products produced were blue powder in the amount of only 0.5 per cent of the zinc distilled, and converter slag.

In processing nickel silver and clean scrap brass, there was only an insignificant amount of dross removed from the melting furnace. This was screened and the metallics were returned directly to the furnace, the pulp being discarded as of no value.

The slag produced from melting oxidized and dirty scrap brass was sent to the dump, the analysis being 0.10 per cent copper, 2.5 per cent to 10.0 per cent zinc, 1.5 per cent iron. The loss of metal to slag represented 0.02 per cent of the copper and from 1.0 per cent to 4.0 per cent of the zinc contained in the charge, the higher zinc loss coming from heavy oxidized scrap.

During the treating of nickel silver, the slag from the converter had the following approximate analysis: copper, 15.0 per cent; nickel, 7.0 per cent; iron, 19.0 per cent; silica, alumina, manganese, zinc, lead, balance.

The slag from the converter when metal derived from scrap brass was being treated was approximately the same as that produced from standard fire-refining operations except that the copper was lower, varying between 15 and 30 per cent, and the iron higher, varying between 15 and 20 per cent.

METALLURGICAL PROCEDURE

Flowsheets

Figure 1 is a flowsheet of the process for the treatment of nickel silver. Fig. 2 is a flowsheet of the process for the treatment of scrap brass.

All metal received was weighed and sampled, after which it went directly to the meltdown furnace or, if necessary, was put through a rotary drier or magnetic separator for drying, grease removal, and elimination of tramp iron.

Melting

The metal was charged to the meltdown furnace in either small bales weighing from 35 to 50 lb. or loose in a special charging box similar in design to the peel of a standard charging machine.

Nickel silver and scrap brass were charged at the rate of 1500 to 2500 lb. per hour, the over-all output being approximately 20 tons per unit per day.

All zinc alloys were melted in a resistor-type electric furnace, designed and operated to furnish a continuous stream of clean molten metal to another resistor-type electric furnace connected in series (Fig. 3). These furnaces are essentially retorts; the details of construction are shown in Fig. 4 and described in detail under the heading of Equipment.

No problems were connected with the melting of the nickel-silver scrap because

this material was relatively free from oxides and foreign matter; this was also true of fired cartridge cases and other relatively clean material. No flux was

times the presence of aluminum or aluminum alloys.

This problem was solved by the use of 5 to 10 per cent rasorite flux, the amount

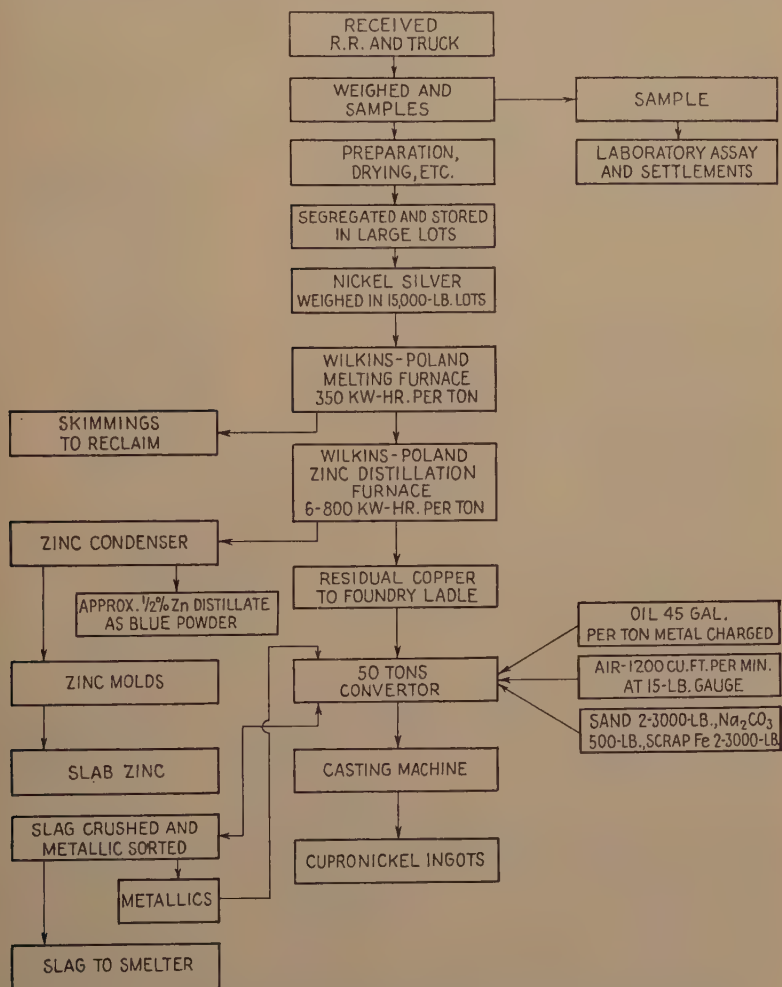


FIG. 1.—FLOWSHEET OF PROCESS FOR TREATMENT OF NICKEL SILVER.

required in the melting of any of this material.

Difficulty was encountered in the melting of refinery-grade scrap brass without excessive loss of zinc by volatilization, because of the presence of oil, grease, water, iron, and other foreign materials and some-

varying with the quantity of oxide and dirt present.

Material such as turnings was dried and degreased in a rotary drier operated with a reducing atmosphere and then passed over a magnetic separator, which permitted rapid melting with the minimum of flux.

While the furnace used for melting in this plant proved satisfactory, it will be recognized that the type of furnace selected for the premelting operation will depend upon the type of material, the cost of fuel or

ing pool on which the dross or slag floated. The dross was removed by skimming or tapping through a door and the slag was removed through a taphole provided for the purpose (Fig. 3).

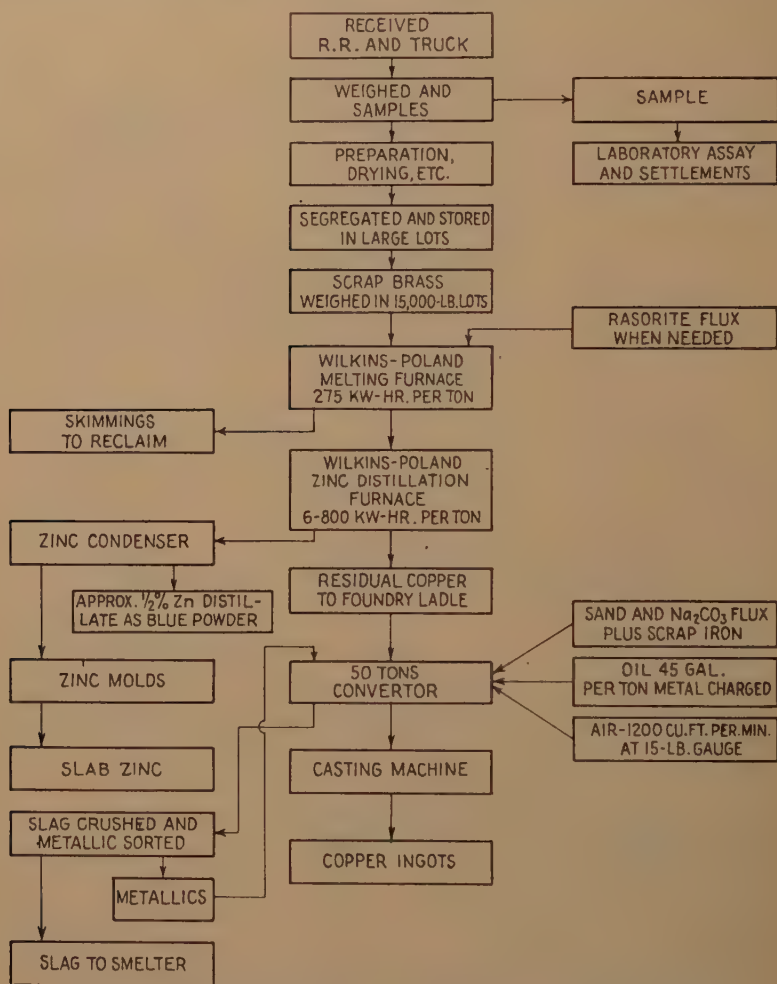


FIG. 2.—FLOWSHEET OF PROCESS FOR TREATMENT OF SCRAP BRASS.

electrical energy, and other factors, and that the novelty of the process and equipment used at Rome does not lie in the particular type of melting furnace used.

A pool of approximately 10,000 lb. of molten metal was kept in the meltdown furnace. This reservoir served as a separat-

Zinc Distillation and Condensation

The large reservoir of molten metal in the meltdown furnace facilitated the delivery of a continuous stream from the meltdown furnace to the distillation unit, which is kept at or near the optimum distillation temperature; i.e., 3200° to 3300°F.

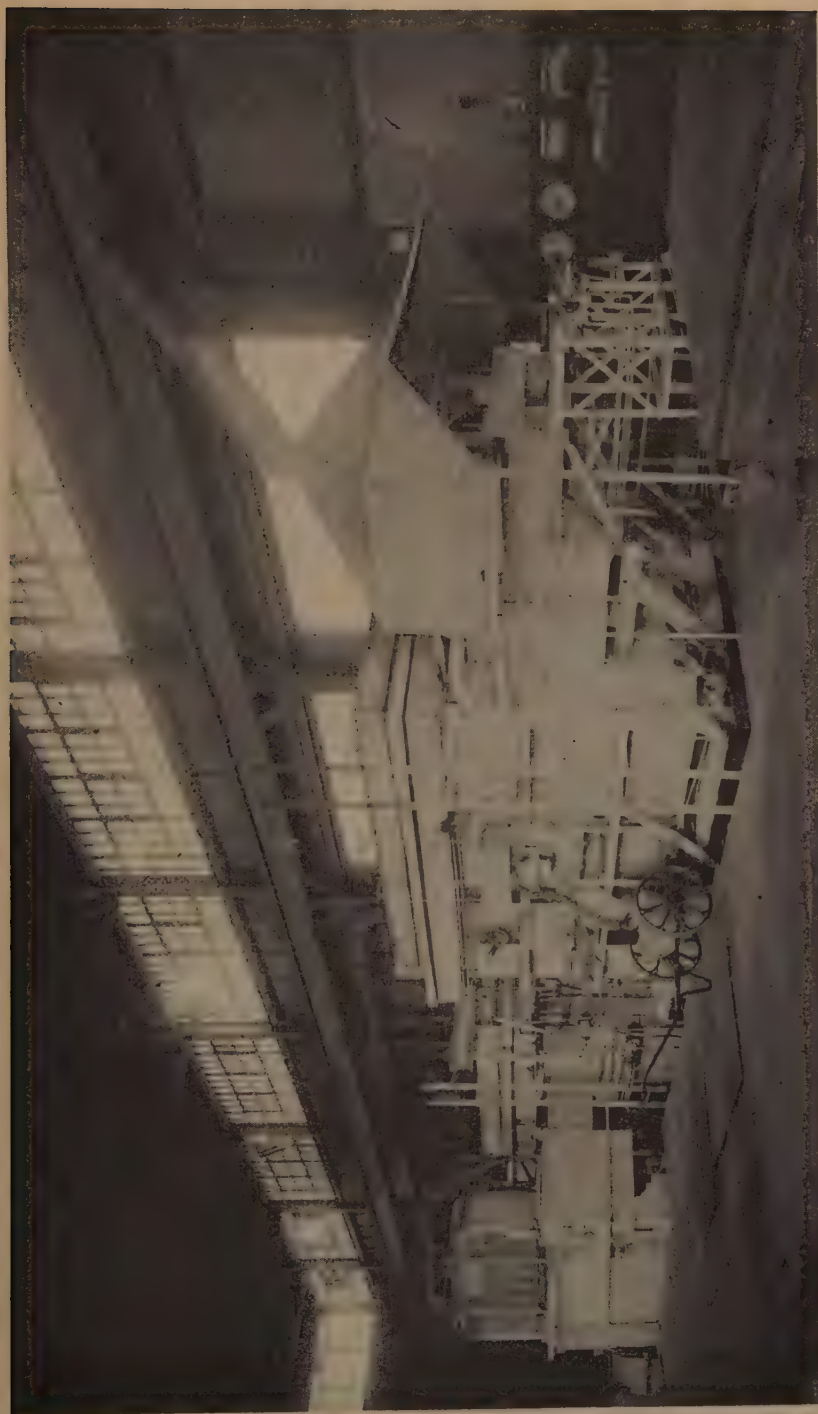


FIG. 3.—ELECTRIC RESISTOR FURNACES IN SERIES.

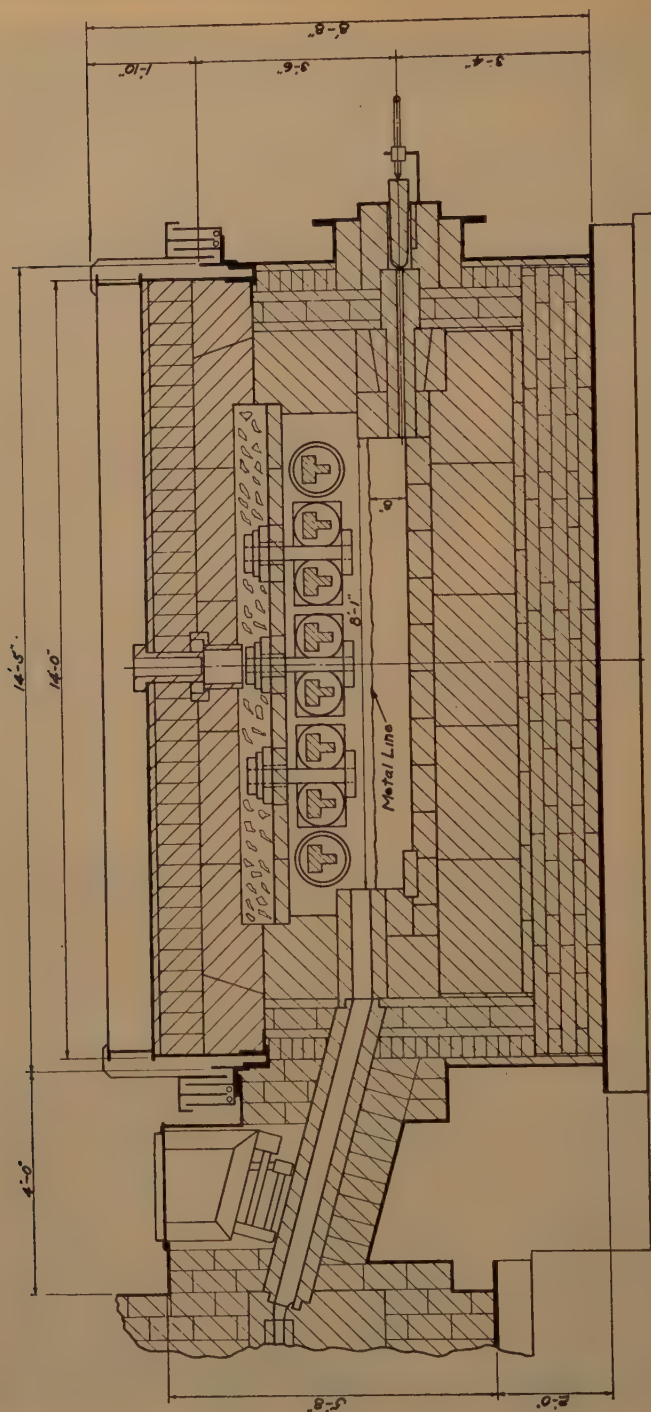


FIG. 4.—LONGITUDINAL SECTION, HIGH-TEMPERATURE FURNACE.

At this temperature a large part of the zinc in the incoming stream vaporized immediately, therefore a constant flow of zinc was delivered to the condenser.

The metal flows from the meltdown to the distillation unit through a carbon tube kept above the melting point of the metal by a small graphite resistor (Fig. 4). A suitable trap is provided to prevent slag or dross from flowing to the distillation unit and to prevent zinc vapor from the distillation unit from entering the meltdown unit.

Through a period of six to seven hours, 12,000 to 15,000 lb. of metal from either nickel-silver or brass scrap were delivered to the distillation furnace (see Equipment). The temperature of this metal during the treating of the nickel silver was 2200° to 2330°F and during the treating of scrap brass, 1850° to 2050°F.

After the predetermined amount of metal had been delivered to the distillation unit, the charging was stopped and the distillation continued until the condenser temperature indicator showed a rapid drop in temperature. At this point the residual metals were tapped into a foundry ladle and transferred to the converter, or cast into shot and stored, if the converter was not operating. The total cycle time per charge was 8 hours.

The metal tapped from the distillation furnace when processing nonleaded nickel silver had the following approximate analysis: zinc, 3.0 to 4.0 per cent; nickel, 15.0 to 19.0; manganese, 0.15 to 0.2; iron, 0.3 to 0.5; copper, balance. The metal from leaded nickel silver had approximately the same analysis, except that the lead averaged about 1 per cent.

The analysis of the residual metal from scrap brass after it had been combined into lots of approximately 50 tons in the converter was zinc 3.0 to 4.0 per cent; nickel, 0.25; iron, 0.50; lead, 1.0; tin, 0.75 per cent; copper, balance.

A constant power input and temperature

were maintained during the distillation period. This resulted in a fairly uniform delivery of zinc to the condenser (Fig. 5) at a temperature approximately the same as the distillation temperature, i.e., 3200°F., and a slight positive pressure in the furnace as indicated by a gauge glass connected to the oil seal.

The zinc vapor entered the condenser at one end above the maximum level of the zinc allowed to collect on the bottom. Liquid zinc was tapped intermittently from the opposite end, the time interval between tapings being approximately one hour.

It is well known that the problems in designing and operating zinc condensers to obtain the maximum of liquid zinc and the minimum of blue powder become more difficult as the partial pressure of the zinc vapor delivered to the condenser is decreased, and it will be recognized that in this operation they are at a minimum because of the delivery of practically 100 per cent metallic vapor to the condenser.

Virtually all of the noncondensable gases from the furnace lining are eliminated in the initial heating of the distillation furnace, and after the first charge the condenser vent is sealed.

The condenser is air-cooled. It is rectangular in shape, the inside dimensions of the principal radiating portion being 4 ft. 6¼ in. long, 1 ft. 2¼ in. wide, 3 ft. 6 in. high, built of standard 9-in. carborundum brick laid up and cemented together with carborundum cement to make a 4½-in. wall. The cover was made of 3-in. graphite plates cemented into a steel pan with carbonaceous cement. This cover was cemented to the top and held down with steel saddles and tie rods. The bottom was of insulated crucible construction designed primarily to hold approximately 1000 lb. of liquid zinc.

This condenser had a maximum capacity of approximately 700 lb. of zinc per hour

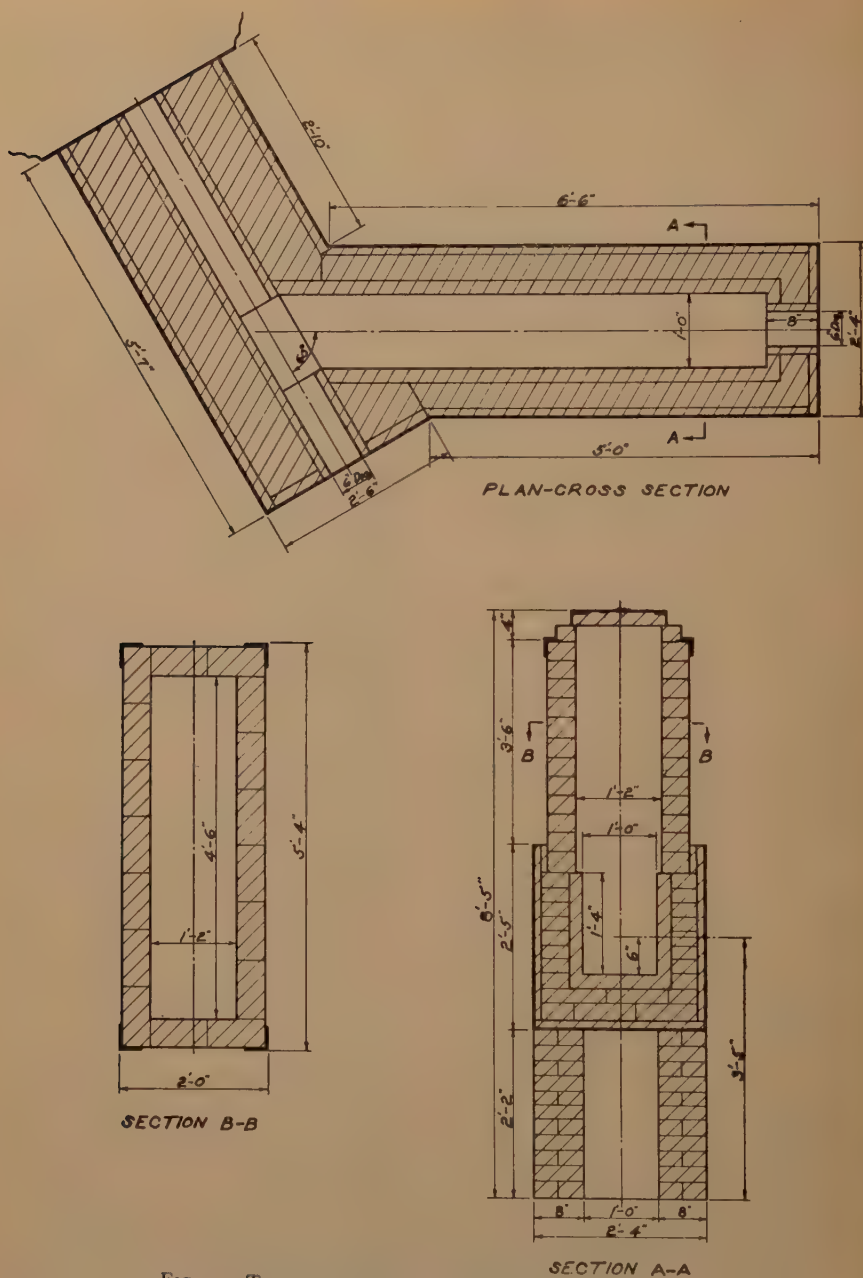


FIG. 5.—THE CONDENSER; PLAN AND CROSS SECTIONS.

and operated satisfactorily down to approximately 100 lb. of zinc per hour. It was only necessary to place insulating panels on the side of the condenser to cut down the radiating surface when operating at very low zinc rates. More than 99.5 per cent of the zinc was condensed as liquid metal.

The temperature at the top of the condenser, as indicated and recorded from a thermocouple inserted at this location, proved to be one of the most useful means of supervising and controlling both the melting and distillation furnaces. From this temperature record, all delays in charging, the relative rate of charging, the end of the zinc distillation and, consequently, the proper time to tap the residual metals, could be detected.

At the start of a furnace campaign the condenser was preheated with gas burners to approximately 400°F. During the tapping period between charges the temperature would fall to approximately 500°F. During distillation the temperature varied between the melting and boiling points of zinc, depending upon the rate of zinc delivery to the condenser. There were no difficulties in obtaining liquid zinc throughout this entire temperature range.

Converting Residual Metals

Each converter charge consisted of 50 tons of molten metal or shot from the distillation furnaces, the charging and meltdown operations requiring approximately 16 hours.

When treating residual metal from low-lead nickel silver, the blowing and skimming operations required 5 hr.; pouring and casting 3 hr. In charges containing lead there was an additional refining time of approximately 4 hr. Little or no flux was used on nonleaded furnace charges, but on all leaded charges approximately 2000 to 3000 lb. of sand and approximately 500 lb. of sodium carbonate was used as a flux.

With the leaded material, the blowing was continued until a sample dissolved in nitric acid showed an insoluble residue of nickel oxide. At this point approximately 2000 to 3000 lb. of scrap iron was charged. This iron acted as a reducing agent and reduced the nickel and copper oxides in the slag to metal.

After the metal in the converter was finally skimmed, it was covered with charcoal and green poles were used for agitation and reduction as in standard copper refining.

The operation of the converter when treating residual metal from brass scrap was approximately the same as for the copper nickel except that the control during blowing was by means of determinations of microscopic oxygen.

THE PLANT AND EQUIPMENT

The Rome plant was designed to produce 500 tons of cupronickel ingots per month from nickel-silver alloys.

All equipment was installed in a standard crane runway building 260 ft. long by 75 ft. wide. The entire area was serviced by two 10-ton bridge cranes. The converter had a potential capacity of approximately 1200 tons per month.

The receiving, weighing, and metal-preparation equipment was of standard type of the required capacity.

The distillation furnace (Fig. 4) was a major development that made the process practical and commercially economical. This furnace is essentially a retort heated internally by electricity. The resistor operates in an atmosphere of zinc vapor generated at the distillation temperature. The furnace was designed to operate up to 3500°F. and it is believed that modifications can be made that would make it practical for temperatures up to 4000°F.

This furnace consists of a gastight $\frac{3}{4}$ -in. thick steel tank, 14 ft. $5\frac{1}{2}$ in. long by 9 ft. $9\frac{1}{2}$ in. wide by 7 ft. 3 in. deep, lined with suitable refractories, and is

constructed so that the roof is removable. The joint between the roof and the hearth section of the furnace is sealed with sand and oil seals. The hearth is approximately 9 ft. 0 in. long by 5 ft. 0 in. wide and has a depth of 18 in. below the lead-in terminals. The holding capacity of the furnace is approximately 7 tons of copper. The furnace hearth, side walls and roof are of heavy carbon blocks backed up with fire clay and finally with insulation. The combination is proportioned so that the outside steel temperature would be 350°F. with the furnace temperature at 3300°F. The combination of high temperature, metallic vapors, and the need for a perfectly sealed furnace presented many refractory problems. However, they were all solved and some of the units have been in use for a period of two years with relatively low maintenance expense. In the selection of the refractories particular attention was paid to the coefficient of expansion because the furnace is built into an airtight steel tank with no provision for expansion other than the compressibility of the insulating refractories.

The drawing shown as Fig. 4 is a longitudinal section of the furnace showing the refractory lining, insulation, connection to meltdown furnace and means of heating, resistors and graphite cover between the resistors and the roof. The manner of supporting the resistors is not shown in the drawing. These are supported from saddles resting on the top of the graphite cover and insulated with sintered pure alumina.

The 7-in. space between roof and graphite cover is filled with charcoal as a heat insulator.

The removable roof is made of five pieces of carbon that extend the full width and are supported by fire-clay skewbacks. The carbon pieces are keyed and cemented together, as are all other parts of the carbon lining, for the purpose of inhibiting the free access of zinc vapors to the back-up refractories.

Many minor features of the construction are of considerable importance to its successful operation, for instance, the tap hole. The tapping arrangement as finally developed consists of a graphite nozzle and stopper, the stopper being held firmly in place by an external steel screw and yoke. In operation there is a small amount of graphite-clay mixture used as a sealing compound around the base of the stopper after it has been put in place. The same material is used to seal off the stopper from the outside atmosphere. With simple tools designed for the purpose, this lute material is removed just prior to withdrawing the stopper from the nozzle and is replaced after the nozzle has been put in place for the next charge.

Fig. 3 is a photograph showing a meltdown and distillation unit, zinc condenser, charging arrangement, slag tap, and electric controls, of one unit at the Rome plant. In this arrangement a furnace similar to that described for the distillation but without the zinc condenser is used for melting down the material, tapping off the dross, slag, and so forth. In this unit the metal overflows from the melting furnace to the distillation furnace in a continuous stream, through a trap that prevents the zinc vapor in the distillation furnace from escaping to the meltdown furnace.

Fig. 6 shows the tapping end of the distillation furnace, the outlet of the zinc condenser, the foundry ladle and fume hood.

Fig. 7 shows the charging arrangement as equipped for charging baled materials manually, also the location of the temperature-control and power-control panels.

The heating elements of the electric meltdown and distillation furnaces consist of a graphite grid made from dense low specific resistance graphite. In the particular distillation furnace being described the resistor consists of eight tee-shaped elements, each approximately 5 ft. long

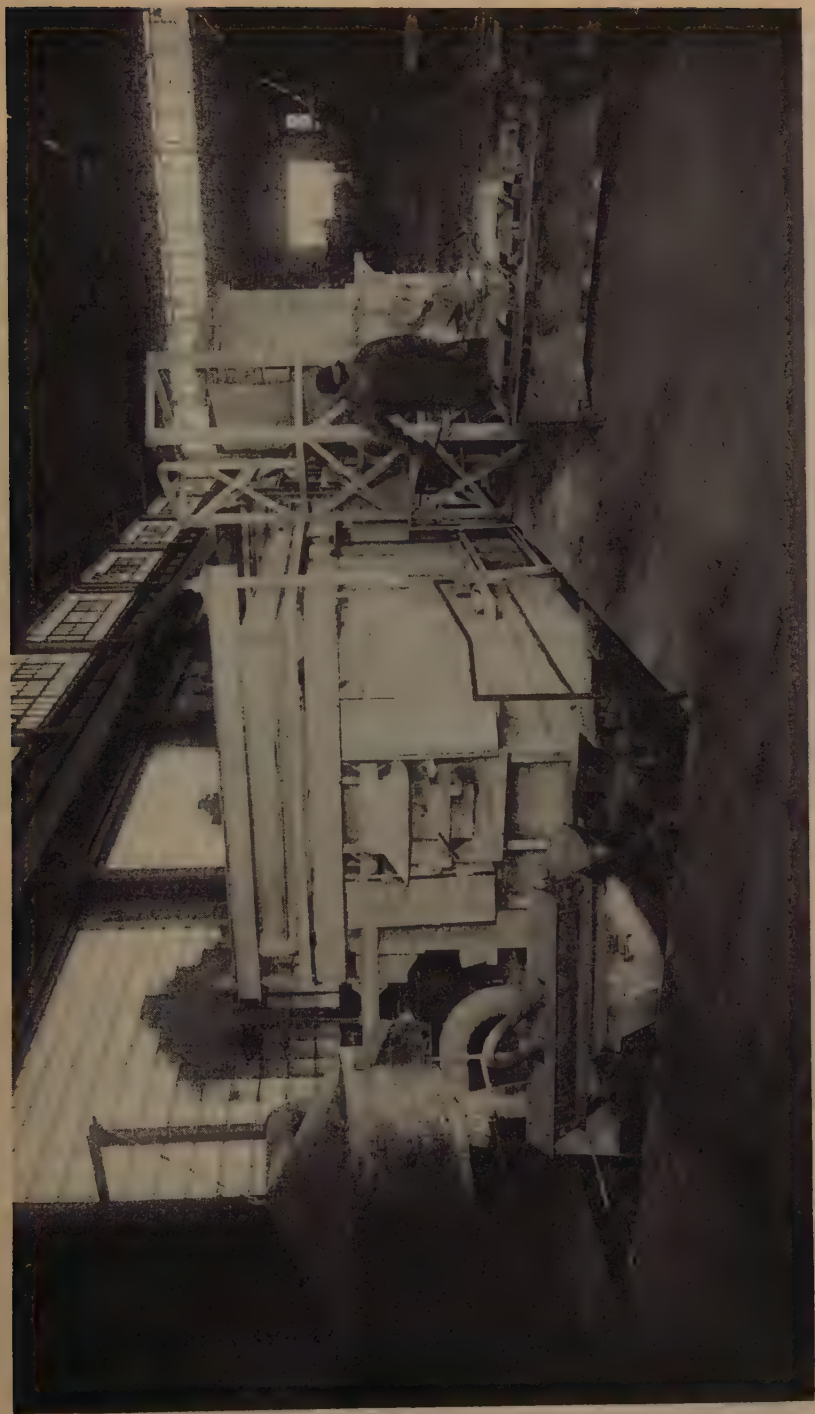


FIG. 6.—TAPPING END OF DISTILLATION FURNACE.

with a cross-sectional area of 20 sq. in. The total resistance of the resistor including the lead-in terminals is approximately 0.007 ohm at operating temperature.

The furnaces shown in Figs. 6 and 7

Custom-designed water-cooled copper terminals, machined from solid pieces of copper, are used for making connection to the graphite lead-in terminals on the furnace.



FIG. 7.—CHARGING ARRANGEMENT EQUIPPED FOR CHARGING BALED MATERIALS MANUALLY. CONTROL PANELS AT RIGHT.

are each rated at 750 kva. The transformers are 750 kva., standard impedance and are provided with standard accessories. The high-voltage winding is extended with taps to give the following low voltage at reduced kilovolt-ampere capacity: 80/75/70/65/60/55 volts. These taps are connected to a ratio adjuster with operating handle available from floor level and provided with an interlock. The transformer is placed as close as practical to the lead-in terminals of the furnace so that the self-induction reactance of the bus bars may be as low as possible.

The bus bars are of standard construction, the cross section calculated on the basis of carrying 1000 amp. per sq. in. of cross-sectional area.

The cabinet containing the furnace-control panel is near the furnace, and on its door is mounted a voltmeter, an ammeter, and a control switch with indicating lights for operation of the feeder circuit breaker.

The temperature of the furnace is recorded by a radiation pyrometer. The optical unit of the pyrometer sights on a standard roof target block. In operation the temperature changes of the furnaces are slow. Consequently power-input control is of the all-on, all-off type.

The converter was of special design, having a holding capacity of 50 tons. The bottom of the furnace was circular; the rest of the furnace was standard reverberatory construction except that four 1¼-in. diameter tuyeres were installed along one

side. The furnace was tilted on trunnions by hydraulic rams. Provision was made to lower the furnace approximately 27 in. from the neutral position and to raise it 6 ft. 6 in. for casting the metal direct to the pouring spoon on the casting machine. The bottom and side walls of this furnace were lined with 13½-in. magnesite brick. The roof was of fire clay. The converter was oil fired with an oil burner having a capacity of 75 gal. per hour.

The combustion gases and fume were delivered to a brick-lined hood that connected to a stack that was 5 ft. in diameter by 125 ft. high.

The tuyeres were supplied with air from a 15-lb. per sq. in. electric blower supplying 1200 cu. ft. per minute.

Almost all the magnesite brick work was still serviceable after two years of service, the only exception being that several repairs were made in the tuyere zone, where steel-clad 18-in. magnesite brick was finally installed.

There was some difficulty in the beginning of the operation in keeping the tuyeres punched, but this was alleviated to a considerable extent by reducing the number of tuyeres to three and increasing the air velocity about one third.

ECONOMICS

The initial investment necessary for building a plant to recover metallic zinc and refined copper from the type of materials described would be appreciably less for this process than for any of the existing processes. It is estimated that this type of plant would cost less than half the amount necessary for the old processes. The big saving in investment is due to the elimination of cooling flues, baghouses, and electrolytic-zinc or retorting plants for the conversion of zinc oxide to metal.

A complete plant, including site and having the capacity to treat 750 tons of nickel silver or 750 tons of scrap brass, was

built at Rome, N.Y. in 1942-1943 for approximately \$750,000.00.

The operating costs for receiving, weighing, sampling, drying, and all other operations up to molten metal ready for distillation are all the same, whether this process or another process is used.

The items of cost of particular interest in connection with the new process are as follows:

The distillation furnace, including zinc casting, requires:

Labor.....	1¼ man-hr. per ton
Power*.....	600-800 kw-hr. per ton
Repairs and supplies..	\$2.00 per ton
Overhead, taxes, and other expenses depend upon local accounting.	

Converting and casting requires:

Labor.....	3 man-hr. per ton
Oil.....	45 gal. per ton
Repairs and supplies..	\$4.25 per ton
Overhead, taxes, etc. as noted above.	
Miscellaneous labor..	2½ man-hr. per ton

SUMMARY

1. A new process in which metallic zinc is recovered directly from nickel silver and secondary copper-base metals, such as scrap brass, has been developed and described.

2. Nickel silver was converted by this process and equipment to commercial cupronickel, used by the U. S. Navy for condenser parts.

3. The process and equipment described materially reduces the investment and size of the plant needed to recover metallic zinc from nickel silver, scrap brass, and other secondary sources.

4. A high-temperature electric resistor furnace is described, which was developed for the distillation of zinc from copper-base alloys. This furnace is believed to be a new and valuable metallurgical tool. It has been

* Power required for distillation runs between 560 and 650 kw-hr. per ton, but is shown as above to include initial heating of furnace, any delays and Sunday holdovers.

considered for use in the melting and refining of primary and scrap aluminum, magnesium, copper and copper alloys; the distillation of zinc from galvanizers' dross and silver-zinc skims from the Parke's lead-refining process; also, the treatment of by-products in the production of ferro-silicon. It may also find a field in the sintering of certain of the carbides and other high-melting-point metals and metallic compounds in large batches rather than

in the relatively small batches now being processed.

ACKNOWLEDGMENT

Grateful acknowledgment is made to R. A. Wilkins, Vice-President in Charge of Research and Development, Revere Copper and Brass Incorporated, Rome, N.Y., without whose assistance, support and faith in the project, final success would not have been achieved.

Effect of Length of Cycle on the Economics of Retort Zinc Smelting

By B. M. O'HARRA,* MEMBER AIME AND F. G. McCUTCHEON†

(New York Meeting, March 1947)

UNTIL about 1930, the universal practice of horizontal-retort zinc smelters in the United States, as far as the writers are aware, was to operate the retort furnaces on a 24-hr cycle; that is, the retorts were charged in the early morning of one day, and in the early morning of the following day the residues were cleaned out, the retorts recharged, and a new cycle started.

During the business depression of the early thirties, zinc production fell off to the extent that zinc smelters had idle retort capacity. Rather than continue to run some of the retort furnaces on a 24-hr cycle and shut down the remainder, a few companies decided to try out a longer cycle. Although the output of zinc per retort per day is lower, the longer cycle permits a larger charge per retort and improved zinc recovery.

Advantages of the longer cycle were soon evident, and the practice spread rapidly. Various lengths of cycle were used, typical examples being 28-hr, 32-hr, 36-hr, and 48-hr. The 48-hr cycle fits in best with the standard routine of smelter practice that was built up on the basis of the 24-hr cycle; that is, the retort furnace "maneuver" always comes at the same time of day, and can be performed in the cool hours of the early morning.

Under some conditions, particularly in some of the older plants, where the retorts are smaller than in newer plants, a 48-hr cycle is longer than necessary, and some intermediate length of cycle may theoretically be most economical. Use of an intermediate cycle, however, means that the maneuver comes at different times on consecutive days, and that sometimes it comes during the hottest part of the day.

The work on the retort furnaces is extremely hot and arduous at best, and it is much worse, of course, if it is done during the heat of a summer day. When labor was plentiful and tractable, many plants were able to operate on cycles of intermediate length, but the workmen did not like the working hours. Under present labor conditions, it is hardly practicable to operate with a cycle of intermediate length, so the choice has narrowed down to the alternatives of 24-hr or 48-hr cycles.

In any discussion of economics, too comprehensive generalization is not warranted, because local conditions affecting economics vary greatly. The best economic practice at one plant at any given time may be uneconomical at another plant, or even at the same plant at another time. To determine the length of cycle that is the better practice at a given plant at a given time requires a weighing of the advantages and disadvantages of each cycle, taking into consideration all the local conditions.

Some of the factors that must be considered in making the comparison are discussed briefly in the following paragraphs.

Manuscript received at the office of the Institute Dec. 24, 1946. Issued as TP 2156 in METALS TECHNOLOGY, April 1947.

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CAPITAL INVESTMENT AND AMORTIZATION CHARGES

If we assume the condition of ample excess retort capacity to operate on a 48-hr cycle without sacrifice of tonnage, capital charges can be neglected, since they will be the same for a given tonnage treated, whether in a smaller or larger number of retorts.

Capital charges can similarly be neglected for a plant that has been largely amortized in the past, and on which current amortization and depreciation charges are small; that is, it holds true unless there is some other compelling reason for treating a tonnage of concentrates greater than the capacity of the plant on a 48-hr cycle.

If it becomes necessary to treat a tonnage of concentrates that is greater than the capacity of a given plant at the 48-hr cycle, there is the choice of operating on a shorter cycle or building new retort blocks. In that case the capital charges on the additional investment must be weighed against the economies of the longer cycle. This balance will vary greatly for different plants; for example, the cost of a new retort block at a plant using producer gas as fuel, including the additional gas-producer capacity and waste-heat boiler or regenerative chambers, is much greater than at a natural-gas plant where only the retort block itself is required.

As previously noted, the practice of cycles longer than 24 hr first came into vogue at a time when there was excess retort capacity. During the war years, however, the demand for plant capacity caught up with the supply, and in some instances at least, it was found preferable to build new blocks to furnish additional 48-hr capacity rather than return to a 24-hr cycle.

MARGIN OF PROFIT PER TON CONCENTRATES TREATED

Assuming a plant with a fixed number and size of retorts, and concentrates available beyond the capacity of the plant when

operating on a 48-hr cycle, the choice between 24 and 48-hr cycle will be affected by the margin available between the cost of the concentrates and the value of their zinc content, to cover treatment cost, zinc losses and profit. Often this margin is so low that the difference between 48-hr and 24-hr cycles is the difference between profit and loss; in such cases, the choice is clear. As the margin of profit per ton increases, however, the point may be reached where the 24-hr cycle with a smaller profit per ton but a greater tonnage will give a greater total profit than the 48-hr cycle with a larger profit per ton but smaller tonnage.

During the thirties the margin between the price of zinc concentrates, particularly Joplin concentrates, and the value of their zinc content was small. This further encouraged the adoption of the 48-hr cycle during those years.

During prosperous years, as the price of zinc rises, the tendency is for the smelter margin to rise also, and the demand for smelting capacity increases. These factors work in favor of the 24-hr cycle. On the other hand, as the price of zinc goes up, the value of the additional recovery obtainable by the 48-hr cycle increases, and this works in favor of the latter.

PROFIT ON BY-PRODUCT CADMIUM AND SULPHURIC ACID

In considering the margin of profit per ton concentrates, as in the discussion just preceding, the profit on the by-product cadmium and sulphuric acid produced per ton of concentrates must be included for zinc smelters that recover such by-products.

For illustration, let us assume two zinc smelters with sufficient concentrates available to operate at capacity on either 24-hr or 48-hr cycle, and with all conditions similar except that one has a sulphuric acid plant and the other has not. Let us further assume that the zinc-smelting operation

alone shows a profit on 48-hr cycle operation but a loss on 24-hr cycle operation. Then the plant with no sulphuric acid recovery can operate at a profit only on a 48-hr cycle. For the other plant, however, the profit on the additional by-product sulphuric acid that can be produced by treating the larger tonnage of concentrates possible with a 24-hr cycle may more than offset the loss on the smelting operation with the 24-hr cycle; in the case of this plant the 24-hr cycle could then give the better over-all profit.

SOURCE OF CONCENTRATE SUPPLY

For a smelter operating on purchased concentrates, the comparison of 24-hr versus 48-hr cycle can be based on the comparative profits of the smelting plant alone. If, however, the smelter treats concentrates from the company's own mines, the effect on the mine profits also must be considered. If the mines can profitably produce more concentrates than the smelter can treat with a 48-hr cycle, and have no other equally good market for the concentrates, the smelter may have to operate on 24-hr cycle even if the effect on the smelter profit is adverse.

WAEZ PLANT

The comparison between 24-hr and 48-hr cycle operation may differ decidedly, according to whether or not the zinc smelter has a Waelz plant for treatment of the retort residues. In the absence of a Waelz plant, the zinc left in the retort residues is either completely lost or only partly recoverable by means of a gravity concentrator. With a Waelz plant most of the zinc in the retort residues is recoverable (though at additional treatment cost); it may conceivably be more profitable to operate with a 24-hr cycle and be satisfied with comparatively low direct recovery, leaving the unrecovered zinc in the residues to be recovered by the Waelz plant.

In the normal method of operating on

24-hr cycle, about 6 to 7 pct of the zinc in the charge is lost as uncondensed fume, as compared with only 2 or 3 pct in normal operation on a 48-hr cycle, and this, of course, is permanently lost. In operating on 24-hr cycle in conjunction with a Waelz plant, the aim should be to cut down this fume loss and leave more zinc in the residues, even though this may mean a lower direct recovery of zinc by the retort furnaces.

SIZE OF RETORTS

The relative economy of 24-hr and 48-hr cycles depends to some extent on the size of the retorts. As already stated, 48 hr is longer than necessary for the maximum economical recovery when using the smaller retorts characteristic of some of the older zinc smelters in the United States. While the writers cannot cite accurate figures to prove the point, it is undoubtedly true that there are several hours when the furnaces are consuming gas and labor of attendants without making sufficient additional recovery to pay for the extra fuel and labor.

To obtain the full benefit of the 48-hr cycle the retorts should be large enough so that the full 48-hr period is required to give the optimum balance between zinc recovery and treatment cost. The writers believe that, for Joplin concentrates and natural-gas fuel, this size has about been reached by some plants with retorts having an internal volume in the neighborhood of $2\frac{1}{4}$ cu ft each. This optimum size may vary with the nature of the concentrates treated, the efficiency of the furnace labor, and other local conditions.

COST OF FUEL

The amount of heating fuel consumed per ton of concentrates is greater for the 48-hr than for the 24-hr cycle, though not as much greater as might be assumed. This is a definite disadvantage of the 48-hr cycle,

and the disadvantage is greater the higher the unit cost of fuel.

The consumption of reduction fuel per ton of concentrates, on the other hand, is less for the 48-hr than for the 24-hr cycle. Therefore, the advantage of the 48-hr cycle increases with increasing cost of reduction fuel.

LABOR RATES

The man-hours of labor for discharging residues, charging and accompanying operations (the so-called "maneuver") is less per ton of concentrates for the 48-hr cycle than for 24-hr, because of the heavier charge per retort. This is partly but not wholly counterbalanced by a greater amount of labor for attendance during the remainder of the cycle. The over-all labor per ton concentrates is less for the 48-hr cycle, hence the advantage of this cycle tends to rise with increasing labor rates.

GENERAL EXPENSE

The distributive, indirect or general expense tends to remain about the same for a given plant (though not entirely so), regardless of the tonnage treated.

For a plant having excess retort capacity, so that the available tonnage could be treated on either 24 or 48-hr cycle, the general expense per ton concentrates would remain approximately the same for either cycle. In operating a plant at full capacity, however, the general expense per ton concentrates would be greater for the 48-hr cycle, because the total tonnage treated would be smaller.

DETAILED COMPARISON OF ZINC RECOVERY AND DIRECT OPERATING COSTS

Having discussed in a general way certain factors that have a bearing upon the relative economy of 24-hr and 48-hr cycles, we can undertake a more detailed comparison of zinc recovery and direct operating cost with the two cycles. This comparison necessarily is based largely on the authors'

personal experience at the plants with which they were connected during the period when the transition from 24-hr to 48-hr cycle was being made, though they have had opportunity to visit other plants and discuss the subject with other zinc metallurgists.

The plants with which we have had personal experience during this period are the zinc smelter of the Eagle-Picher Mining and Smelting Co. at Henryetta, Okla., and that of the Arkansas Smelting Co. at Van Buren, Ark., the latter being a subsidiary of Eagle-Picher.

Both of these plants use natural gas as fuel for heating the retort furnaces, and chiefly Arkansas semianthracite as reduction fuel. Both are comparatively old plants, having small retorts (approximately 1.75 cu ft internal volume at Henryetta and 1.6 cu ft at Van Buren). The furnace blocks at both plants have 800 retorts each. Some new blocks were built at Henryetta during the war, but for the sake of uniformity the size of retorts in the new blocks was not altered greatly from that of the old ones. The retorts at both plants were made with the old-style augur presses, though a hydraulic press has since been installed at Henryetta. Clay retorts containing approximately 25 pct silica flour were used.

The comparative data on 24 and 48-hr cycles are mostly from operations during a period of several years before and during the early part of the recent war. This was before zinc-smelting costs had sky-rocketed as they have in the past few years. During the period in question the concentrates treated at both plants were exclusively from the Tri-State (Joplin or Picher) district. The charge to the retorts was sometimes sintered flotation or mixed flotation and coarse concentrates, sometimes dead-roasted coarse concentrates, and sometimes a mixture of the two. Since these various types of charge behave somewhat differently in the retorts, some judgment must

be exercised in choosing data from the operating records for comparison.

Neither smelter had a Waelz plant during the period in question, though one has since been built at Henryetta. During most of the period the retort residues were concentrated on jigs and tables and the concentrates were returned either directly to the retort charge or to the roasters or sintering machines. The discarded condensers were similarly concentrated and the concentrates returned to the retorts. For a period of something over a year the retort residues were shipped to a Waelz plant at Cherryvale, Kansas, for treatment.

The comparative data on the 24-hr and 48-hr cycles are to some extent from the simultaneous operations of different blocks in the same plant on the different cycles, but to a greater extent are from different periods of time when a whole plant was operated on one or the other of the cycles. Since so many other conditions affect the operation of zinc furnaces, and these are never exactly the same at different times or on different blocks at the same time, comparative data on the two cycles cannot be put forth as giving a precisely accurate comparison, but only a close approximation to it. Furthermore, the comparative picture thus shown may not be an accurate representation of what the comparison would be at some other plant, where other conditions—for example, size of retorts or type of concentrates treated—may be decidedly different.

In the following pages costs will be discussed in terms of quantities of fuel, hours of labor, and so forth, rather than in terms of dollars and cents, since unit costs for fuel, labor, and other items vary so greatly that costs expressed in monetary value have only fleeting significance.

ZINC RECOVERY

Zinc recovery cannot be singled out and discussed as a separate item independent of other factors. Up to some

limiting point, zinc recovery can be improved by reducing the weight of sinter or calcine charged per cubic foot of retort volume, but this leads to increased treatment cost per ton. Conversely, operating cost per ton can be reduced by increasing the charge, but at the expense of reduced recovery. At some point there is a balance between zinc recovery and treatment cost per ton, which gives the optimum economic result.

Several years ago one of the authors calculated that under the conditions existing at Henryetta at that time a 1 pct increase in the weight of charge at a lowered recovery of 0.3 pct would be about an even break. As far as the charge could be increased without a sacrifice of recovery greater than indicated by that ratio, there was an economic advantage in doing so. This ratio may differ at other times or at other plants.

It is not always easy to determine just what the point of optimum balance is between density of charge and recovery. Under the conditions existing at Henryetta and Van Buren during the period when the two cycles were under comparison, our best judgment was that the optimum balance for the 48-hr cycle when the plant was operating properly was at a furnace recovery of 91 to 92 pct, including the recovery from recirculated condenser concentrates and residue concentrates. For this recovery the charge was in the neighborhood of 39,000 lb of sinter or calcine in a furnace ($1\frac{1}{2}$ block) of 400 retorts at 1.75 cu ft per retort, or about 56 lb sinter or calcine per cubic foot. This is exclusive of the weight of residue and condenser concentrates returned to the charge currently as produced.

For a period of something over a year in 1940 and 1941, when the residues, instead of being wet-concentrated, were shipped to a Waelz plant, the charge weight was increased by 1000 to 2000 lb per furnace. The direct furnace recovery

without the return of residue concentrates dropped to about 89 pct, but the over-all recovery, including the zinc recovered from the Waelz plant fume, was about 95 pct.

For the 24-hr cycle the optimum balance between weight of charge and zinc recovery is even more difficult to fix, because variations in the weight of charge have an even greater effect on zinc recovery and cost per ton, and also because variations in the efficiency of the furnace work and other conditions cause greater variations in recovery. The 24-hr cycle does not provide the "margin of safety" that the 48-hr cycle does. We considered that the optimum economic result was obtained at a furnace recovery of 87 to 88 pct with a charge of about 28,000 lb of sinter or calcine for a furnace of the size mentioned above, or 40 lb per cubic foot.

(With inefficient labor, furnaces in poor condition, or other unfavorable factors, it may be difficult to attain as good results as this with the 24-hr cycle. A three-months campaign with one block at Henryetta on 24-hr cycle during the first quarter of 1946 showed a greater disparity between 24 and 48-hr cycles than is indicated by the foregoing data. The average difference in recovery was 7.67 pct. We understand that another zinc smelter in the natural-gas field had a similar experience. In such cases the natural metallurgical differences between the two cycles are augmented by the attitude of the furnace crew toward the 24-hr cycle. Having become accustomed to the 48-hr cycle, they dislike the shorter cycle, with its much greater accompaniment of heat and smoke from the furnaces, and tend to "buck" any return to it. Furthermore, inefficient labor on a furnace operating on a 24-hr cycle has a greater effect in the way of lowered recovery than it would with 48-hr cycle, because of the lower "margin of safety" of the shorter cycle. However, even the

48-hr cycle suffers from present-day inefficient labor, and to hold the recovery shown by the data given above the charge per cubic foot of retort volume may be as much as 10 pct less.)

Data for 28 and 32-hr cycles comparable to those given for 24 and 48-hr cycles were about as follows:

Cycle	Sinter or Calcine, Lb per Cu Ft	Furnace Recovery
28-hr.....	45	89-90
32-hr.....	46-47	90-91

The optimum balances indicated by the preceding data are not necessarily the optimums at other plants or at the same plants at another time when other conditions may differ radically.

Some zinc smelters with newer blocks and larger retorts have been able economically to attain considerably higher recoveries with 48-hr cycle—up to 95 pct, according to report. With larger retorts the charge per furnace can be large enough for good operating cost without the weight per cubic foot being so great as to make good recovery difficult.

The weight of charge per cubic foot has an upper limit beyond which any attempt to increase it necessitates decreasing the reduction fuel below the amount necessary for good reduction. Where the size of the retort is limited some inexpensive method of physically compacting the charge, such as a "chaser," might warrant a trial.

COST OF FUEL

Heating Retort Furnaces

At Henryetta and Van Buren the retort blocks were not equipped with individual gas meters, so strictly accurate comparative data on gas consumption for cycles of different lengths are limited. However, by a process of elimination, particularly at times when most of the

other plant operations were temporarily closed down, a fairly reliable comparison could be made.

The gas consumption (approximately 1000 Btu gas) for a furnace block of 800 retorts, of 1.75 cu ft capacity each, was about 700,000 to 725,000 cu ft per day on a 48-hr cycle, or 1,400,000 to 1,450,000 cu ft per cycle. With a charge of 39,000 lb sinter per furnace, or 39 tons per block, equivalent to 47 tons concentrates, this amounts to 30,000 to 31,000 cu ft of gas per ton concentrates. At plants with larger retorts the gas consumption per ton concentrates is considerably lower.

Comparable data for three other cycles are as follows:

Cycle	Gas Consumption per Block per Day, Cu Ft	Gas Consumption per Block per Cycle, Cu Ft	Gas Consumption per Ton Concentrates, Cu Ft
24-hr	900,000	900,000	26,500
28-hr	900,000	1,050,000	27,500
32-hr	830,000	1,110,000	28,500

Reduction

The amount of reduction fuel will vary according to the size of retorts, type of reduction fuel used, and other local conditions, but the following ratios are typical:

24-hr cycle: 0.43 ton reduction fuel per ton concentrates (green ore weight)
 48-hr cycle: 0.30 ton per ton concentrates

These figures include the reduction fuel charged with the blue powder, used for condenser stuffing, retort loam, and other purposes.

RETORTS AND CONDENSERS

With 48-hr cycles the retorts and condensers have a longer life in days but a shorter one measured in cycles. Our experience has been that the larger amount of concentrates treated per cycle just about balances the fewer cycles

per retort or per condenser, so that the cost per ton concentrates for retorts and condensers is about the same for a 48-hr cycle as for a 24-hr cycle or one of intermediate length.

LABOR

Following is a typical illustration of the direct labor requirements for a 48-hr cycle on a furnace of 400 retorts of 700 cu ft total volume capacity:

NUMBER OF MAN
SHIFTS PER FUR-
NACE PER 48-HR.
CYCLE

Maneuver:

1st charger.....	1
2nd charger.....	1
3rd charger.....	1
Hooker.....	1
Bumper.....	1
Chiseler.....	1
Stamper.....	1
Loamer.....	1
Condenser boy.....	1
Shovelers.....	2
Helper.....	1

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Firing and Metal Drawing:

Firemen.....	2½
Metal Drawers.....	3
Stuffers.....	2

7½

Miscellaneous:

Plumber.....	½
Filling new retorts and poking residue chutes...	½
Cleaning molds.....	¼
Water boy.....	¼
Cellar man.....	¼
Sweeper.....	¼
Cleaning castings.....	¼

Total man-shifts per cycle.. $\frac{21\frac{1}{2}}{21\frac{2}{3}}$

Assuming a furnace charge of 39,000 lb sinter, equivalent to about 47,000 lb of concentrates, this works out at about 0.92 man-shift per ton of concentrates. A furnace with larger retorts and con-

sequently heavier charge will require somewhat more labor per cycle, but less per ton concentrates by as much as 10 to 12 pct.

The preceding example is representative of operations several years ago when labor was more efficient than at present. At that time retort residues were shoveled out of the retorts. At present the residues at the same plant are blown out. Under present labor conditions, from one to two more men are required per furnace per cycle for a somewhat smaller weight of charge. Following is a typical example of such a furnace crew:

NUMBER OF MAN-
SHIFTS PER FUR-
NACE PER 48-HR
CYCLE

Maneuver:

1st charger.....	I
2nd charger.....	I
3rd charger.....	I
4th charger.....	I
Bumper.....	I
Chiseler.....	I
Blowout.....	I
Stamper.....	I
Loamer.....	I
Condenser boy.....	I
Gum chisellers.....	2
Helper.....	I
Loam cutter.....	I

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Firing and Metal Drawing:

Firemen.....	2½
Metal drawers.....	4
Stuffers.....	¾

7½

Miscellaneous:

Plumber.....	½
Cleaning molds.....	¾
Water boy.....	¾
Cellar man.....	¾
Sweeper.....	¾
Screening blue powder and melting scrap.....	¾

2.0

Total Man-shifts per Cycle..... 23½

To charge, say, 28,000 lb in the same furnace for a 24-hr cycle will require approximately the same maneuver labor per cycle, and most of the miscellaneous labor will be about the same per cycle. The number of fireman-shifts per cycle will be about half, and that of the metal drawers and stuffers some intermediate figure, but since these latter items constitute a minor fraction of the total labor, the man-shifts, or man-hours, per cycle are not greatly less for a 24-hr cycle than for a 48-hr cycle. Because of the heavier charge for the 48-hr cycle, the cost of labor per ton concentrates is considerably less than with the 24-hr cycle.

OTHER ITEMS OF DIRECT COST

Heating fuel, reduction fuel, retorts and condensers, and labor are by far the principal items of cost in retorting. The differences between the 24-hr and 48-hr cycle for the other items of direct cost have only a very minor effect on the over-all cost.

In connection with the item of repairs, however, it should be mentioned that though the cost per ton for minor day to day repairs does not differ greatly for the different lengths of cycles, frequently there are furnaces in a plant in such condition that they could not long stand the gaff of 24-hr cycle operation without a major rebuilding job, whereas they can be maintained in operation over a long period of time under the less rigorous demands of 48-hr cycle operation. Just what this may amount to in repair cost per ton of concentrates treated during the life of a furnace is difficult to say, but such a situation frequently furnishes an added incentive to 48-hr operation.

DISTRIBUTIVE AND GENERAL EXPENSE

As previously noted, if there is retort capacity available so that the same tonnage of concentrates is treated in a

plant, the cost per ton concentrates for distributive and general expense will be approximately the same for the 24-hr and 48-hr cycles. If, however, the plant can be operated to full capacity whichever cycle is used, then, since the total distributive and general expense for the plant will be about the same for either cycle, and since the plant will have a smaller tonnage capacity on the 48-hr cycle, the cost per ton for distributive and general expense will be greater, in approximately inverse proportion to the smaller tonnage, with the 48-hr cycle.

TOTAL COST PER TON

Under the conditions that existed at the Van Buren and Henryetta plants during the period when the comparisons were made, and with concentrates available to operate the plants at capacity on either 24-hr or 48-hr cycle, the total plant treatment cost per ton, including plant distributive and general expense, but not including general office overhead or capital charges, was slightly lower for the 48-hr cycle than for the 24-hr cycle. That held true for comparisons made over a period of years during which there were considerable variations in labor rates and in unit costs of gas, reduction fuel, and other supplies, but prior to the very large increases that have taken place in the past two or three years.

NET OUTCOME

With operating cost per ton slightly less for the 48-hr cycle, with the much higher zinc recovery from that cycle, and with a small profit margin at best, there was no doubt whatever of the much greater over-all economy of the 48-hr as compared with the 24-hr cycle, though at times the demand for zinc output or smelting capacity necessitated operation of some of the retort blocks

on 24-hr cycle even though it meant a lower smelter profit.

This conclusion does not necessarily hold true for other plants or other times, but, judging by the widespread adoption of the 48-hr cycle, it evidently does hold true under a wide variety of conditions.

The authors hope that this paper will elicit some discussion of the subject from other zinc metallurgists who have had the opportunity to compare cycles of various lengths at other plants and under other circumstances than those which the authors' experience covers.

DISCUSSION

(W. E. Milligan and T. D. Jones presiding)

F. P. SINN*—The paper by B. M. O'Harra and F. G. McCutcheon is an excellent exposition of the subject. It discusses the procedure in great detail and points out and gives due weight to the many variables entering into the problem. Any horizontal retort zinc smelter with this paper before him may translate the data given to his own plant conditions and make a sound decision in regard to his own operation as to the economics for the 48 hr cycle vs. the 24 hr cycle. The authors are to be congratulated.

The results described are those obtained with the use of Joplin ore in retorts having a capacity of 1.75 cf each. The authors point out that the retorts are small for the 48 hr cycle and that plants more recently built or rebuilt with larger retorts have a decided advantage. Most of the economic discussion is based on charge per retort as it should be since the major costs are dependent on the number of retorts rather than their size. In some of the detailed figures given, charge per cubic foot is referred to and certain conclusions drawn. I have dealt with statistical and operating figures stressing charge per cubic foot for more than 41 years and have long since come to the conclusion that stress upon them is more misleading than otherwise. I still inspect cost sheets which show a detailed cost per 100 cf of retort capacity as well as the cost per ton

*The American Metals Co., Ltd., New York City.

of green ore smelted and per 100 lb of metal produced. In my opinion, the cost column per 100 cf of retort capacity would be much more informative if replaced by a column showing the cost per 100 retorts charged. The capital cost involved in the furnace construction, including the furnace buildings, the amount of gas required for firing them and the amount of labor required, are all more directly related to the number of retorts than to their size. The retorts themselves cost more as their size increases and it is true of course that the span of the furnace arch is increased and the length of the tie rods is increased as retorts are lengthened, but these increases in cost are negligible compared to the gain in retort capacity by adding 20 pct to the retort length. The only additional work to be done in the morning maneuver is that of throwing in the additional charge and drawing out the additional residue. If the retorts are blown out with water or withdrawn by machine, the additional residues to be withdrawn may be ignored. The only additional work required of the metal drawers is that of pouring the additional metal produced and making the extra trips of the metal car to the mould stand since the additional metal runs out of the condenser without additional effort on the part of the workman. The major problem in metal drawing is to get the condensers well scraped during each draw and that remains the same regardless of the quantity of metal produced.

The easiest way to increase the size of the retort is to increase the cross-sectional dimension, but I am inclined to believe that for American practice where it is important to use a minimum number of men for cleaning retorts, the maximum cross-section has been reached. I also believe this cross-section may be larger for Joplin ores than for ores higher in iron since the latter ores cause more slagging difficulties. The reason, of course, is that the greater cross-section requires higher furnace temperatures for the final elimination of the zinc due to the poor conductivity of the charge and higher temperatures cause more slag. The only limits to increasing the length of the retorts are those of producing retorts which will withstand the increased span and of getting the charge properly packed in the butt end of the retort. The present day silica retort withstands a much greater span than the old clay

retort and, of course, the carbide retort has the same advantage.

The condenser life with the 48 hr cycle has increased in calendar days, but the consumption per ton of ore used or per ton of metal produced has not improved to the extent expected. This is a matter to be followed carefully and with better scraping of the condensers during each draw, better and more careful cleaning of the condensers during the maneuver and an improvement in the condenser itself, there should be a good chance of improving the practice in this respect.

Professor Hanley asked about the corrosion rate of retorts when using sintered charge and the similar effect in using a non-sintered charge.

The wide use of flotation ores in the zinc smelting industry brought about sintering of those ores. In the beginning it was probably done to increase the porosity of the charge when using a very finely divided roasted ore. The alternative was to use a large proportion of charge fuel coarser in size than otherwise desirable. If the sinter is properly prepared, it is possible to reduce greatly the amount of charge fuel used and, in my opinion, the sinter may be reduced at a lower temperature and with less slagging and corrosion of the retort notwithstanding the smaller proportion of charged fuel present. If by a highly sintered ore Professor Hanley means what I call an over sintered ore, where the sintered particles are slagged, then I think it ought to be made clear that every zinc smelter has found that a particular physical type of sinter gives the best results. It is a little difficult to describe and the smelter finds it out by experience. The means of getting a proper sinter vary with each type of ore and with high iron ores it is sometimes difficult to accomplish. With very pure ores gangue material is sometimes added in small amounts. Generally speaking there is much less corrosion of the retort with a properly sintered ore than with the same ore not sintered, the other conditions being the same. The only possible exception I can think of in this connection is the use of the old Joplin jigged concentrates, but I suspect that even in this case a larger output of metal per retort failure has been accomplished with sintered Joplin flotation concentrates than with the old Joplin jigged material. In making this

statement, I am mindful that over 40 years ago, the M & H plant at LaSalle claimed a 90 day life for retorts, but at that time, the output per retort was small as compared to present practice.

Mr. Schweitzer asked two questions: (1) The relative amounts of blue powder produced in the 48 hr cycle as contrasted with the 24 hr cycle. (2) Whether or not it had been found desirable to segregate the blue powder and reduce it in a separate furnace.

In respect to the first question, I believe the amount of blue powder produced is not very different in the two cases. Perhaps it would be better to state that per ton of metal produced, the amount of blue powder does not appreciably increase with the 48 hr cycle. After considering Mr. Terrell's discussion of this subject, I have given the matter further thought and now wish to state that if an additional metal draw is made for the 48 hr cycle, then there should be an increase in the amount of blue powder produced. In other words, except for the factor of additional metal draws, the amount of blue powder should vary with the amount of metal produced with any given ore, other factors being equal. If in the attempt to charge more sintered ore per retort in the retorts receiving sinter too little charge fuel is used, then undoubtedly there will be an increase in the amount of blue powder produced. As a matter of fact, at one plant with which I am concerned, the number of retorts per block set aside for blue powder etc., is the same for the 48 hr cycle as for the 24 hr cycle. It may be that with the slow firing, less blue powder is made per pound of metal during the greater part of the cycle and that this offsets largely the additional blue powder produced due to the extra metal draw made.

The second question as to the desirability of reworking blue powder in a separate furnace has been a live issue throughout my connection with the industry and probably for a much longer period. In some types of furnaces, temperature control is such that certain retorts are necessarily kept at a slightly lower temperature than the others. In this case the blue powder is charged in these retorts and the average efficiency of the furnace is thus maintained. With the natural gas fired furnaces in the Southwest, this is not necessarily so since with proper regulation of the gas and air, all

of the retorts in the furnace may be maintained at approximately the same temperature. There it becomes a question of cost of handling the materials to another location. It is of interest to know that during the past year, one plant in the Southwest gave the suggested procedure a thorough trial. The plant operated 3 or 4 blocks on straight sintered ore and resmelted all the so-called blue powder products on a separate furnace. The practice there has been discontinued since the additional cost of handling the materials more than offset the other advantages. Although I am not certain about it, I understand also that the practice resulted in a higher consumption of natural gas, which is to be expected.

This raises the question of smelting blue powder by a different method. In Germany the Thede Process has been used successfully for this purpose. The feed, however, is largely prolong zinc dust containing 95 pct metallics. A high recovery is obtained in the form of slab zinc approximating 90 pct of the metallic zinc in the feed. The furnace consists of a rotating heat resisting cast iron drum lined with $2\frac{1}{2}$ in. of fire clay brick containing a small amount of silicon carbide grain. The cast iron shell is one meter in diameter, 2 meters long and 3 to 4 cm thick. The revolving drum is heated from the outside and liquid metal is formed by attrition at a working temperature estimated to be about 450°C within the closed drum.

The Thede Process is described in detail in Final Report No. 379, Item No. 21 entitled The German Zinc Smelting Industry reported by the British Intelligence Objectives Subcommittee Zinc Smelting Mission following its investigation of The German Zinc Smelting Industry in the Fall of 1945.

The Thede furnace is apparently a further development of that by F. Tharaldsen of Norway who developed many years ago at Trollhättan, Sweden, a brick lined revolving furnace heated within by a single continuous high resistance carbon electrode. This furnace operated on the product of the electrothermic furnaces at Trollhättan and recovered as metal 65 pct of the ingoing blue powder which averaged about 70 pct zinc in metallic form.

Because of the difference between prolong blue powder and Trollhättan blue powder, so far successfully treated in this type of furnace, and the so-called blue powder produced by

American horizontal retort smelters, considerable experimental work will probably be required to determine the usefulness of this method to American smelters. It is my understanding that one American smelter experimented with this process some years ago, but I have not heard that it has been used commercially for converting to metal the so-called blue powder resulting from horizontal retort smelting.

The authors of the paper under discussion make the following statement, "The weight of charge per cubic foot has an upper limit beyond which any attempt to increase it necessitates decreasing the reduction fuel below the amount necessary for good reduction." This statement would coincide with my experience had the authors substituted "good recovery" or "good condensation into metal" for "good reduction." It has been my experience that if the carbon in the reduction fuel approaches the theoretical amount required for reducing the zinc present, too much blue powder or zinc dust is produced and too little metal. The condenser becomes clogged with this formation, but if the channel for escape of the gases is kept clear, actual reduction of zinc in the charge progresses to a surprising degree. This oxidation of the zinc vapor is due, I believe, to too much CO_2 present in the gases, as a result of the incompleteness of the so-called gas producer reaction, which is the conversion of the CO_2 formed by zinc reduction back to CO by carbon before too much zinc is reoxidized. If smelters using the 48 hr cycle have an increase in their blue powder production beyond that to be expected by an extra metal draw and the increased metal produced, then it is perhaps due to the use of too little fixed carbon in the charge. The balancing of the extra space gained for sinter by using less charge fuel, and the space required for the extra blue powder resulting therefrom, can only be obtained by trial and error and, of course, the loss in recovery of zinc by reworking the extra blue powder is a part of the equation to be balanced.

A. D. TERRELL*—The paper covers the subject very well and represents pretty much the experience of the other smelters that went from a 24- to a 48-hr cycle.

* National Zinc Co., Inc., Bartlesville, Okla.

The maximum temperature needed in the laboratory of the furnace is less on the 48-hr cycle, and this in turn is conducive to better retort life.

The National Zinc Co., Inc. at Bartlesville, Okla., charge each end of a block of furnaces every other day, instead of alternating the whole blocks, as is done in other natural gas plants. This method of charging has worked out very satisfactorily for us.

The term "Blue Powder" as used in horizontal retort zinc smelting covers a multitude of sins: ladle skimmings, samples from the mouths of retorts, condenser cleanings, floor sweepings, and in some instances, additional reducing fuel. This all goes to make up the so-called "blue powder" part of the furnace charge. It has been the general experience that the number of retorts charged with blue powder is a little greater on the 48-hr cycle. The amount of blue powder made varies considerably with the efficiency of labor.

I concur in the statement Mr. Sinn made, that the condenser loss is exceedingly high on the 48-hr cycle and is a problem which greatly concerns us all, and one which everyone is endeavoring to improve.

K. A. PHILLIPS*—At one or two retort smelters using Hegeler furnaces the "contract" work of the condenser cleaner or connie boy includes the hauling of all or part of the condensers from a central kiln to the furnaces. The connie boy then has a personal interest in keeping the condenser usage at a minimum, and his own work plus his influence upon the other furnace men who handle condensers combine to yield a longer condenser life.

H. C. SCHWEITZER†—*1st Question:* Are any data available regarding the influence of the length of the retort cycle upon the amount of blue powder produced per cycle?

The 48 hr cycle is certainly uneconomical for the smelting of blue powder as we all know that blue powder requires only low furnace temperatures and can easily be treated with maximum recoveries within 24 hr. As a matter of fact, the blue powder retorts are frequently exhausted after 16 to 20 hr of the cycle.

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† Associated Metals & Minerals Corporation, New York City.

This being so, and considering that, according to the American practice where no prolongs are used, a large portion (often up to 30 pct) of the retort capacity is tied up by recycled blue powder, the question arises whether it might not be advisable to collect the blue powder of several furnaces and to treat it in a furnace exclusively charged with blue powder and operated with the 24 hr cycle. This would have the advantage that the furnace capacity of a smelter can be increased considerably (possibly by as much as 10 to 12 pct) by operating with a 48 hr cycle all furnaces charged exclusively with sintered ores, while operating with a 24 hr cycle some furnaces the retorts of which would be charged exclusively with blue powder collected from all furnaces in operation.

Of course, this method will present two disadvantages: (1) the recovery control of each individual furnace will be more difficult until sufficient data and experiences have been secured; and (2) the collection of the blue powder and its transfer to different blocks will result in some additional expenses.

However, the writer feels that by proper organization of this work and by distributing the blue powder furnaces favorably within the group of all furnace blocks in operation, or by using the oldest blocks for the low temperature blue powder operation, the advantages will exceed the disadvantages.

Mr. Francis P. Sinn answered that the length of cycle has no noticeable influence on the amount of blue powder produced, and that the procedure suggested above regarding the separate treatment of the blue powder has been tried for some time by one smelter but has been abandoned due to the increased labor costs involved by the blue powder transfer from one furnace to another.

2nd Question: At the present high price

level, and, particularly, in view of the high price and the scarcity of cadmium, it might be worthwhile to reconsider whether, at least temporarily, and under special local conditions, it might not pay to use again prolongs at the end of the retort mouth. This procedure will, of course, only be interesting for smelters operating with a 24 hr cycle.

The advantages of this procedure will be: (1) the recovery of an otherwise lost cadmium-rich zinc dust (representing approximately 0.7 to 1.2 pct of the total zinc output) which can be used advantageously as precipitating agent in the cadmium plants; and (2) the furnace capacity will be considerably increased due to the fact that the blue powder production will generally be cut by as much as 40-60 pct with a corresponding increase of the direct metal recovery. This latter advantage has, according to the opinion of the writer, been somewhat overlooked when the old European practice of the use of prolongs has been abandoned at a time when labor costs rose and metal prices dropped. (3) The hygienic working conditions will be greatly improved as the prolongs catch most of the smoke which is particularly disturbing during the first 8 to 12 hr of each cycle.

The disadvantage of this procedure is again the additional expense for handling prolongs and dust. However, these costs can be kept within limits if the prolongs are used only until the first (or, possibly, the second) metal draw, as experience has shown that, during the first 8 to 10 hr of the cycle, 70 to 80 pct of the total zinc dust formed during the whole length of cycle is collected in the prolongs.

The writer feels that, under such conditions and if properly applied, the advantages of the use of prolongs will, in some cases, outweigh the additional costs even considering the present high wage level.

Quantitative Spectrographic Determination of Minor Elements in Zinc Sulphide Ores

By LESTER W. STROCK

(New York Meeting, February 1944)

METALLURGISTS handling lead and zinc ores have long been familiar with the spectrograph as a routine analytical tool, as its earliest regular use by American industry was in controlling impurities of zinc metal and its alloys. This application has been extended to other metal industries on an extensive scale, accompanied by refinements of procedure to such an extent that a large part of some metals produced, especially magnesium, aluminum and steel, are checked only by spectrographic methods for conformity to specifications.

The spectrographic analysis of ores and other poorly conducting powdered solids presents difficulties not encountered with metallic samples, which can be arced or sparked as self-electrodes or can be readily dissolved, so that their solutions can be analyzed, as in the American Society for Testing Materials standard methods for zinc and zinc-base alloys. Spectra of powdered solid samples can be prepared by using carbon electrodes provided with a crater of suitable size, into which the sample is packed.

Ore samples and many other powdered solid materials usually analyzed in the chemical and metallurgical laboratory are more complex and varied in composition than samples of metals produced in large tonnages. More preliminary work therefore is usually necessary in devising

a spectrographic method for analyzing a given type of powdered sample than for analyzing metal samples, in order to use that method with confidence. The knowledge that the standard samples and unknowns produce equivalent line intensities at equal concentration is the fundamental basis of any quantitative spectrographic method. On the other hand, powdered samples have an advantage over metals in that any desired number of chemical compounds can be mixed dry in any desired ratio to produce a synthetic standard. Experience has shown, however, that spectra of elements in finely divided compounds introduced into a standard in preparing a synthetic ore sample do not always behave in the electric arc in a manner that produces spectral line intensities similar to those observed at the same concentration in a natural mineral. In ore samples minor elements frequently are contained in the crystal lattice of larger particles of an abundant ore mineral. Their dissociation and volatilization from the sample into the arc then proceeds differently in the standard and sample, with resultant differences in intensity.

During the past 10 years I have devised and applied several quantitative spectrographic methods for determining various elements in rocks and minerals in connection with studies on their geochemistry,¹ but the incentive has gradually changed since the summer of 1940 to the specific practical problem of searching for domestic sources of rare and strategic metals. The

Manuscript received at the office of the Institute, Oct. 3, 1944. Issued as TP 1866 in METALS TECHNOLOGY, April 1945.

* Spectrochemical Laboratory, New York State, Saratoga Springs Commission, Saratoga Springs, N. Y.

¹ References are at the end of the paper.

same methods have been expanded for analyzing ores and their products wherever they are important to war production. Zinc sulphide ore concentrates is one of the types of ore to which I have recently applied those methods.

This winter (1943-44) more than a dozen concentrate samples were secured, which represent large-tonnage production of ore from important districts in the Western Hemisphere, which furnished an opportunity to experiment with a general quantitative method for determining as many elements as possible in commercial zinc sulphide concentrates. Several problems still remain unsolved, but the progress made is presented in order to illustrate the value to the zinc-ore industry of quantitative spectrographic analysis.

It should be noted that many data exist in the literature that are not referred to in this paper, because emphasis is placed here on the new quantitative spectrographic method developed and not on the specific analytical results obtained on definite ore and mineral samples.

My experience and interest in the use of the spectrograph for determining the several rare and minor elements associated with zinc sulphide began at Oslo in 1937, where I was instructing assistants in the Norwegian Department of Commerce Raw Materials Laboratory in quantitative spectrographic methods. As one practical problem, the semiquantitative spectrographic analysis of Norwegian zinc sulphides was taken up by I. Oftedal,² who has since published many details of his results. As I have compared my analytical results on ZnS concentrates with Oftedal's results on isolated ZnS minerals, I have mentioned him several times in the following pages, but this does not imply that he has been the sole worker to study the distribution of minor metals in natural zinc sulphide. Results by other workers will be referred to in a later paper, con-

cerned primarily with the *results* of analyses rather than with the *method*.

DEVELOPMENT OF QUANTITATIVE D.C. CARBON ARC METHOD

In principle the spectrographic method of analysis is very simple. A sample is burned in the d.c. carbon arc, the spectral lines emitted are photographed, and their intensity is then used as a measure of concentration of the elements producing the lines.

Internal Intensity Standard and Buffer

Maximum accuracy and reproducibility are obtained by determining relative intensities in photographed spectra rather than absolute intensities. For this purpose a line of some element present in constant quantities in the sample is selected as an intensity standard. Since lines of the most abundant elements present are not always sufficiently constant and reliable as standards, it is usually necessary to incorporate some element into both standards and samples to serve as an internal intensity standard. The element selected for this purpose must naturally be absent from all samples to be analyzed and not produce lines that interfere with the lines of elements to be determined. It should be a minor constituent of the sample arced yet sufficiently large to mask any trace of very faint coinciding lines that might appear in occasional samples. An ideal circumstance would be to provide an intensity standard line of similar wave length for each line whose intensity is sought, especially when, as in zinc sulphide ores, the lines of all elements determined are scattered over an interval of nearly 1000 Å. in the ultraviolet. This is in general impractical, and would increase the time and labor per analysis out of proportion to any improvements in accuracy.

In the method used in this work, each standard and sample were mixed with four parts of carbon powder and one part of an

intensity standard buffer mixture consisting of 0.1 per cent BeO in NaCl. This buffer mixture has several advantages. The arc spectrum of beryllium consists of very few lines, and these do not coincide with lines of other elements in the ZnS ores; and the line Be 3130.42 for 0.1 per cent BeO is known to vary linearly with concentration and lies well above the spectral background. It is thus a usable intensity standard. Moreover, its wave length is intermediate between the several wave lengths used for the elements determined, so that it affords the very desirable possibility of a single intensity standard for all other lines involved. The NaCl diluent was selected as a buffer because of the presence of varying amounts of other constituents in the concentrates which, like NaCl, are known to lower the arc temperature and disturb the uniform dependence of intensity on concentration from sample to sample. It also creates an arc that greatly enhances the intensity of several rare-element lines to a point where their accurate measurement is possible, especially those of gallium and indium. However, NaCl creates less favorable conditions for determining lowest concentrations of cadmium, antimony, mercury, and perhaps bismuth. Carbon powder was used to prevent the formation of a melt bead, which is difficult to burn to completion without serious loss of sample, and also to minimize the usual fractional distillation from the arc.

Concentration Standards for Metals to Be Determined

The preparation of a single set of standards to cover the concentration range of all elements observed in zinc sulphide ore concentrates presents some practical difficulties, especially since many contain up to 10 or 12 per cent Fe. This produces many lines in the sample spectra, some of which disturb or coincide with lines of other elements. Then, too, it is necessary

that one standard contain at the same time a few thousandths of one per cent of some elements (e.g., In, Ga, Ge) and a hundred or a thousand times this amount of other elements (e.g., Cu, Pb, Mn). Obviously, the preparation of a homogeneous dry mixture of this nature is not an easy matter, even when pure sulphides of all elements are available.

To overcome the difficulty of mechanically mixing dry powders in such extreme ratios, an "impurity stock" was prepared by a combination of precipitation and evaporation. For this purpose a solution of all elements to be introduced into the dry standards was prepared from the purest salts and metals available, in a predetermined ratio corresponding with their average ratios to be expected in concentrate samples. The solution, contained in a Vitreosil dish, was slightly acidified, and a known amount of high-purity ZnS was added. Since the amount of ZnS was large compared with the volume of impurity stock solution, it remained as an undissolved sludge into which other elements were precipitated as an intimate mixture on addition of H_2S . When this mixture was evaporated, other elements present, such as Ni, Co, Mn, and unprecipitated traces of all the rest (Cu, Pb, Sn, Sb, Ga, In, Tl, Ge, Ag, Hg) would crystallize out in the sulphide paste. After drying, careful removal of all solids from the dish, weighing and calculating of the actual percentages of each element present (from known weight added and total weight of the product), this mixture was used as "impurity stock A" in preparing one series of standards. Nine individual standards, prepared from it, represented $\frac{1}{2}$, $\frac{1}{4}$, $\frac{1}{20}$, $\frac{1}{200}$, $\frac{1}{600}$, $\frac{1}{2000}$ and $\frac{1}{6000}$ of this impurity stock in a base consisting of 1 per cent SiO_2 , 1 per cent $CaCO_3$, 10 per cent FeS and 88 per cent special high-purity muffled zinc sulphide. The special ZnS was prepared in the New Jersey Zinc Company's Research Laboratory, and I

am indebted for it to Messrs. M. L. Fuller and G. W. Standen. Impurity stock A contained the following metals, largely as sulphides, the remainder being ZnS:

	WT. PER CENT		WT. PER CENT
Pb...	6.25	Sn...	0.500
Mn...	3.75	In...	0.355
Cu...	2.50	Ga...	0.305
Cd...	2.50	Tl...	0.250
Co...	2.50	Hg...	0.250
Sb...	0.557 (partly lost)	Ni...	0.250
Ag...	0.518	Ge...	0.218 (partly lost)

These standards were then combined with the intensity standard and buffer, already mentioned, and two different series of d.c. carbon-arc spectra were prepared. One series was made from a large sample arced ($\frac{1}{16}$ -in. by 5-mm. crater), which uses about 60 mg. total mixture, of which 10 mg. is the actual standard and the remainder carbon powder plus buffer; the other from a small sample ($\frac{1}{16}$ in. by 4-mm. crater), which uses about 10 mg., of which less than 2 mg. is the actual standard. The large samples of each standard were arced in duplicate while the small ones were arced in triplicate. The larger sample should, and in most cases does, make it possible to determine a correspondingly lower concentration of each element. The electrode carrying the sample is the cathode throughout this work.

Germanium and antimony were lost by volatilization from the hot acidified impurity solution before precipitation, therefore a second series of standards was prepared by dry-mixing their sulphides. To this "impurity stock B," cobalt and nickel were also added as sulphides, as a check on the precipitated stock used in standards A, where Co and Ni were present largely as chloride and nitrate in a sulphide matrix. Results from both sets of standards agree to within the experimental accuracy.

Preparation of Stepped Sector Spectra

The quantitative results reported in this paper are based on the familiar and conveniently prepared stepped spectra. The spectrographic equipment is essentially the

same as that described in my original operating manual,³ published in 1936. This same publication also outlines details of the photographic photometry procedure in preparing concentration calibration curves from microphotometer measurements made on the photographed spectra.

In this particular work on ZnS-concentrates, a Hilger high-dispersion quartz spectrograph and a Zeiss Spectral Line microphotometer were used. The basic functioning of the stepped-spectrum quantitative method depends on the arrangement of certain simple accessories used with the spectrograph.

It is essential to produce uniform distribution of light from the entire arc over a length of the spectrograph slit somewhat greater than the 10-mm. portion covered by the step sector. Incandescent electrode light is blocked out by an interposed screen on which the objective, placed near the burning arc, focuses the arc image. Only the light desired (arc column plus cathode layer light) passes an aperture in the screen, a selection controlled by proper and constant adjustment of the arc holders while viewing the arc image on the screen. A rotating step sector, placed in front of the spectrograph slit, controls the exposure time along its length and produces seven different exposures of each spectral line, each differing by a factor of 2 from its neighbor. Uniformity of illumination of the slit is achieved by focusing the selected arc image and selecting diaphragm onto the spectrograph prism by means of a second simple lens (longer focal length) placed on the arc side of the sector.

The smaller samples arced ($\frac{1}{16}$ in. by 4-mm. crater) were packed into a carbon electrode (cathode) prepared from a standard $\frac{3}{16}$ -in. diameter high-purity carbon rod by lathing the crater end off to about 3 mm. outside diameter. This type and size of electrode produces a very steady arc, whose "hot spot" covers the entire electrode and sample (especially with car-

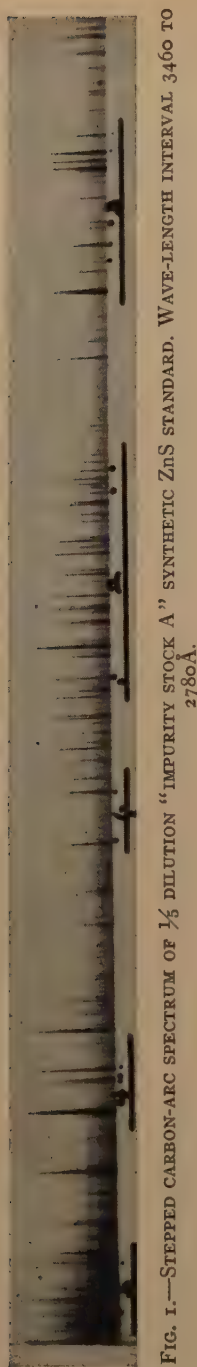


FIG. 1.—STEPPED CARBON-ARC SPECTRUM OF $\frac{1}{2}$ DILUTION "IMPURITY STOCK A" SYNTHETIC ZnS STANDARD. WAVE-LENGTH INTERVAL 3460 TO 2780 Å.

bon electrodes, as distinct from graphite), and in which light and current fluctuations tolerated by most laboratories do not occur. Under these stabilized conditions the small samples often give more intense and uniform spectra than do the larger ones. With large samples, fractional distillation difficulties are magnified. Further, there is irregular loss of light through uncontrollable wandering of the arc, loss of sample through violent spattering caused by intermittent contact of the arc hot spot with sample melt, and serious self-absorption and reversal of lines in a vapor-rich arc column. Some of these difficulties are greatly aggravated when graphite electrodes are used and no carbon powder is mixed with the sample arced.

The general appearance of a stepped spectrum, and the distribution of the several wave-length regions used in the work on ZnS ore is illustrated by Fig. 1. This is a reproduction of the longer wave length, half of one of the six similarly stepped spectra that can be photographed on a standard 4 by 10-in. plate in the ultraviolet (approximate wave-length range illustrated is 3460 to 2780 Å.). The stepped lines on this reproduction may appear, on casual inspection, merely as lines of gradually tapering intensity, but actually are composed of eight discrete and differently exposed steps. This is a spectrum of the $\frac{1}{2}$ "impurity stock" standard, which contained:

	WT. PER CENT		WT. PER CENT
Pb.....	1.25	Sn.....	0.100
Mn.....	0.750	In.....	0.071
Cu.....	0.500	Ga.....	0.061
Cd.....	0.500	Tl.....	0.050
Co.....	0.500	Hg.....	0.050
Ag.....	0.104	Ni.....	0.050

also supplied by standards base (containing 6.35 per cent Fe, 1.0 per cent SiO_2 and 1.0 per cent CaCO_3) Fe, 5.08 per cent, SiO_2 , 0.80, CaO, 0.448.

The intermediate wave-length position of the Be line 3130.42, used as intensity standard, is obvious, being the stronger

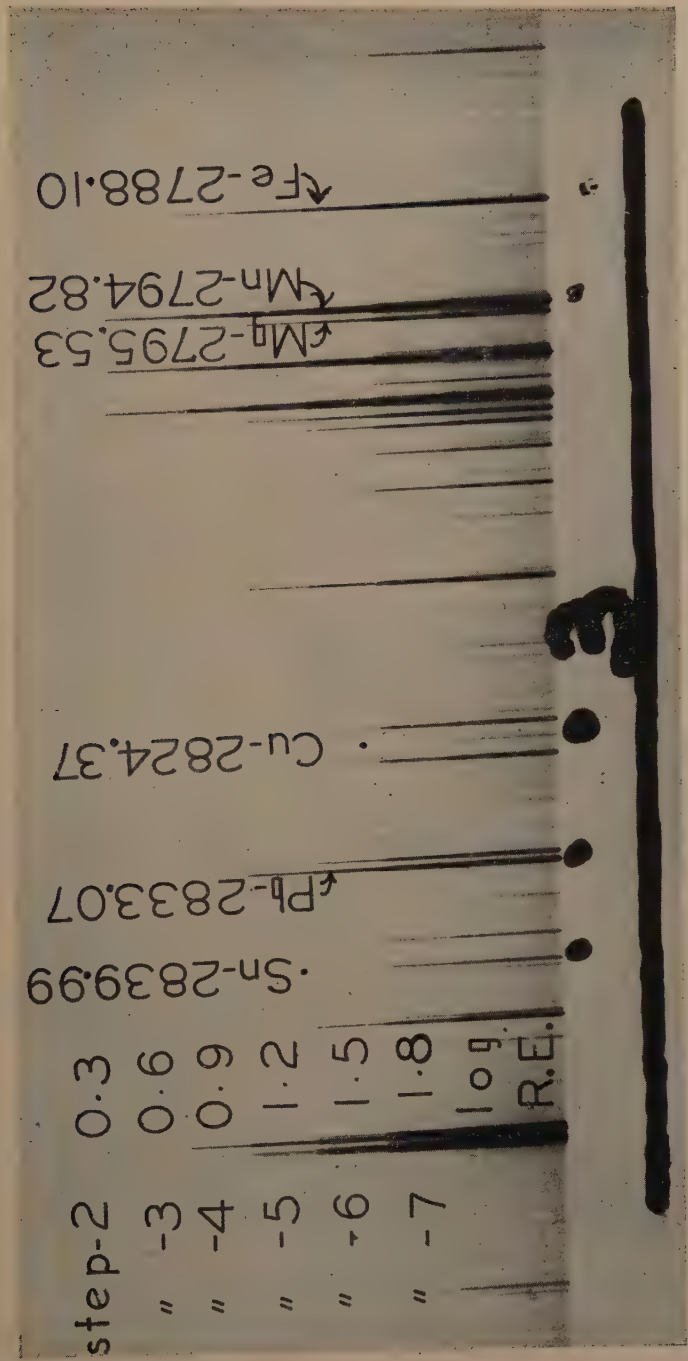


FIG. 2.—ENLARGED PORTION OF STEPPED SPECTRUM OF FIG. 1, SHOWING STEPS OF DIFFERENT EXPOSURE TIME PHOTOMETERED. SHORTEST EXPOSURE-TIME STEP (LOG R.E. = 0.0) NOT INCLUDED.

line of the doublet at the left-hand (longer wave length) end of the No. 1 underlined group in Fig. 1. The individual steps of the stepped spectrum illustrated are shown

densities from the two lines of different light intensity. The Li line is much more intense, and the intensity ratio of the two lines is numerically expressed by $\Delta \log T$,

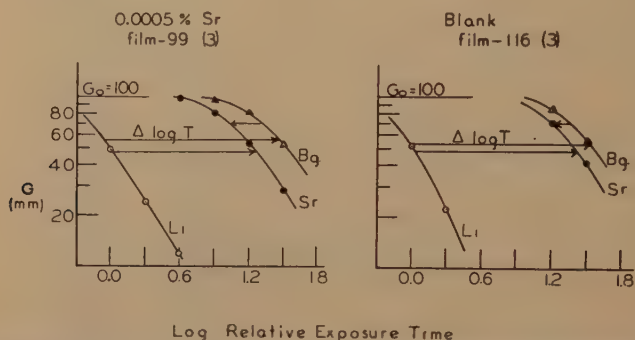


FIG. 3.—DERIVATION OF $\Delta \log T$ (A NUMERICAL INDEX OF THE INTENSITY RATIO OF TWO LINES) FROM PHOTOMETER CURVES OF STEPPED SPECTRA. (From L. W. Strock.⁴)

more clearly in the partial enlargement in Fig. 2. The bottom (densest) band represents full exposure, which was never photometered. Above it lie successively the useful steps, whose logs' relative exposure time (relative to the shortest exposure given by step No. 1, not included in the figure) are 1.8, 1.5, 1.2, 0.9, 0.6, 0.3 and 0.0. The wave lengths of Sn, Pb, Cu, Mn and Fe lines used in this region are noted in the figure.

Derivation of Numerical Concentration Index ($\Delta \log T$) from Photometer Curves of Stepped Spectra

The determination of a numerical index for the intensity ratio of two spectral lines from photographed stepped spectra is illustrated in Fig. 3, reproduced from an earlier paper.⁴ In this illustration the strontium curve is obtained by plotting, on a log scale, actual photometer deflections for several adjacent steps of an Sr line. Its horizontal distance from a corresponding curve derived from the intensity standard lithium line is a numerical index of the intensity ratio of the two lines. It is actually the logarithm of the exposure time ratio required to secure equal photographic

which is measured graphically from the photometer curve. The curve Bg is for the spectrum background, which fixes the minimum limit of $\Delta \log T$, and, of course, also fixes a limit on the decrease in line intensity with concentration—a point of great importance and difficulty ignored by many, the disturbing influence of which will be evident in later illustrations. The position of the Sr curve with respect to the Li line depends on Sr content—moving horizontally to the left (i.e., to lower T) for increasing Sr content and to the right (i.e., high T) for decreasing Sr content. $\Delta \log T$ values need be calibrated only against concentration to produce a curve for analyzing unknowns.

The photometer curves obtained from various lines in the step spectrum reproduced in Fig. 1 are shown as the top series in Fig. 4. Similar curves for a tenfold dilution of this standard are shown in the lower half of the same figure. Comparison of these two series illustrates the resulting shift to the right (to higher log relative exposure-time values) of the curves derived from variable elements in the standards, relative to the standard Be curve, as their concentrations are decreased. A $\Delta \log T$

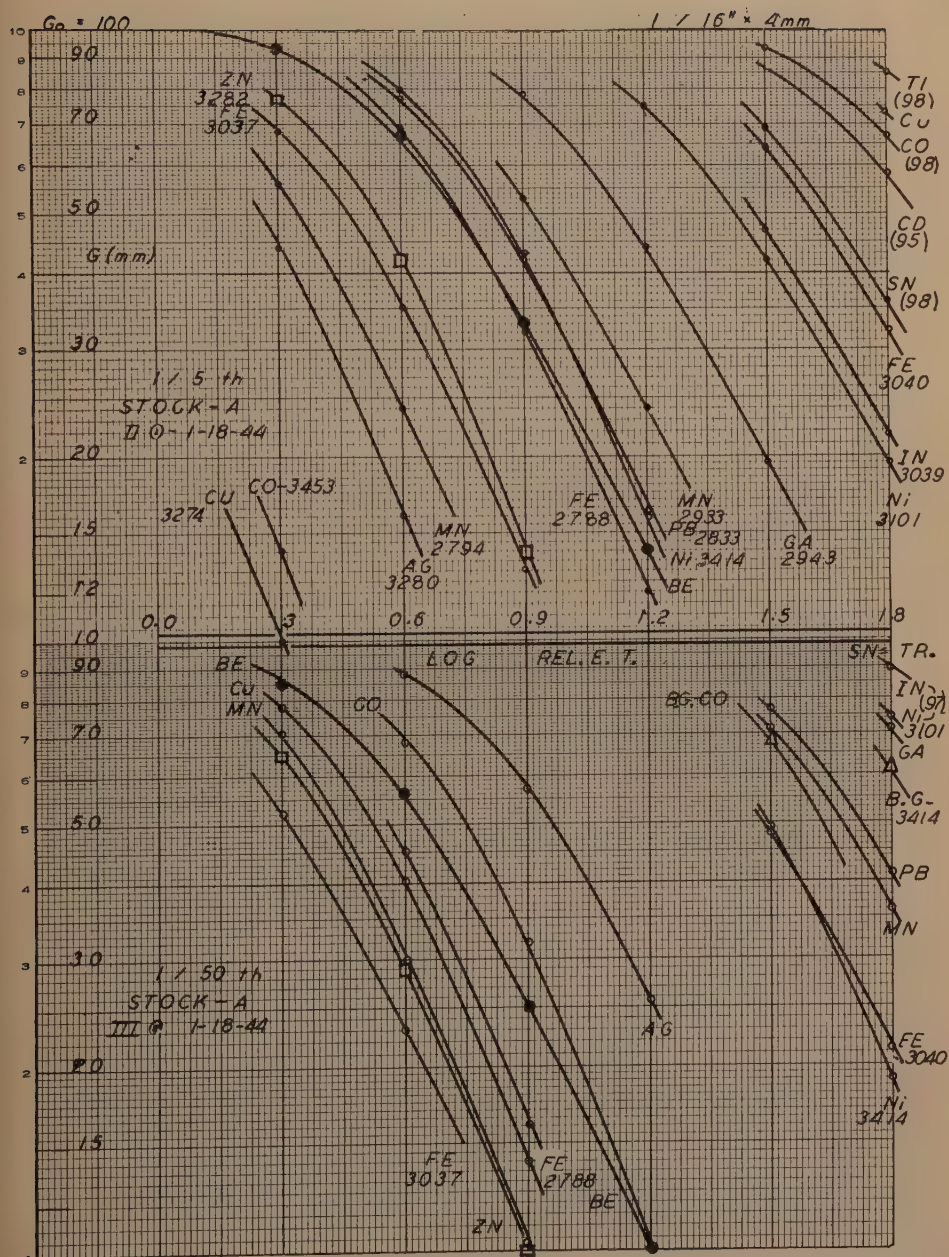


FIG. 4.—PHOTOMETER CURVES OF IMPURITY ELEMENT LINES IN STEPPED SPECTRA OF TWO DIFFERENT SYNTHETIC STANDARDS.

Galvanometer readings G plotted against relative exposure time.

value is obtained for each curve of this family by measuring its actual distance from the intensity standard (Be) curve, at the same $G = 40$ level wherever possible, otherwise at some other convenient level. This distance, measured in the exposure (horizontal) axis unit, is the logarithm of the exposure-time ratio of the two lines at the same density level. $\Delta \log T$ values from curves to the left of the Be curve are conveniently given (+), and those to the right (-), denoting that their parent lines are stronger and weaker respectively than the standard Be line. Mathematically this is the sign of the actual logarithm involved by expressing $\Delta \log T$ as the log of the exposure-time ratio of the intensity standard line to the line of variable intensity. Values of $\Delta \log T$ were secured for each element from all spectra of each standard. The numbers in parentheses at some element's symbols in Fig. 4 are the G values for the background at those lines measured for the elements so designated. The background is measured only when the line is sufficiently faint to be measurably influenced by the background.

The spread in $\Delta \log T$ values from multiple spectra of a given material is a measure of both sample homogeneity and reproducibility of the combined arcing process and photometric procedure. The spread in values for individual standards is evident in Figs. 5 to 12. Actual analyses of samples are averaged from a minimum of three spectra. Duplicate analyses check to ± 2 per cent when $\Delta \log T$ values are about 0.25 or more above background, but not in the self-absorption affected region of the calibration curves.

Over-all accuracy of the method must further allow for possible errors arising from the use of noncomparable or improperly buffered standards and samples. In this ZnS work, the over-all accuracy, as far as determinable, is equivalent to the reproducibility.

Values of $\Delta \log T$ from some usable lines

of each impurity element are obtained, as outlined above, for each standard arced and photographed; which, when plotted against concentration, provide concentration calibration curves over the standard's concentration range. These are the "working curves" for determining the same elements in samples of similar composition by the same analytical technique, which can be applied in a routine manner without further constant reference to standards. These curves also provide quantitative information on most questions that arise as to the usefulness and reliability of a quantitative spectrographic method. The most important of these questions are: reproducibility of results, lowest concentration detectable and quantitatively determinable, effect of disturbing factors such as spectrum background and interfering lines, upper limit of quantitative determination, effect of sample size, mechanical and chemical nature of sample, and effect of other elements present.

STANDARD CONCENTRATION CURVES FROM EXPERIMENTAL $\log T$ VALUES FOR METALS IN STANDARDS

The experimental concentration curves, based on the synthetic standards described in the foregoing pages, are outlined in the following paragraphs for all the spectrographic groups of elements except Tl and Hg. The usefulness and limitation of the method for each element is evident in the curves shown for several of the impurity metals contained in the standards prepared.

Antimony

The experimental ($\Delta \log T$:concentration) curve for antimony is shown in Fig. 5. As mentioned, this is based on the dry-mixture standards of series B, carrying antimony as natural stibnite. The Sb 2877.915 line is relatively weak, so that, as shown by the experimental curve, it can be used up to at least 3 per cent Sb. For the same reason, however, this line does not

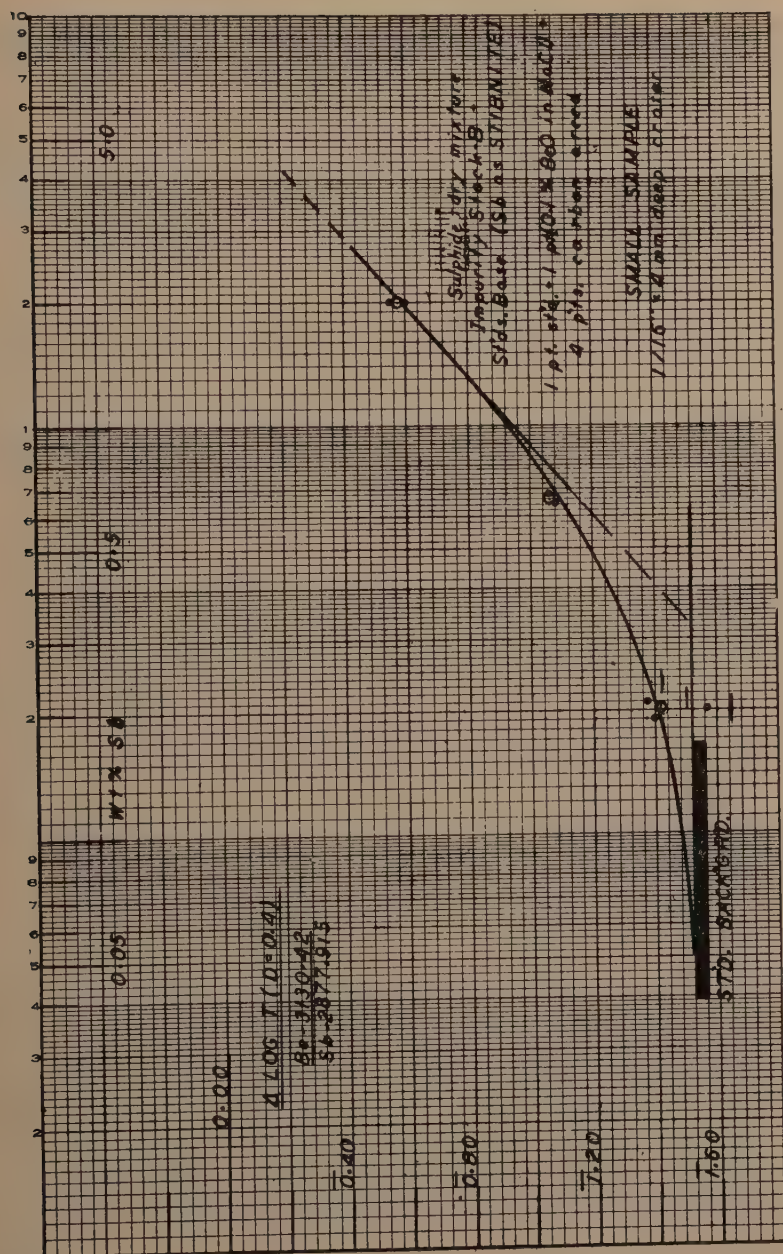


FIG. 5.—CONCENTRATION CALIBRATION CURVE FOR Sb 287.915 LINE IN SYNTHETIC ZnS ORE STANDARDS.
 $\Delta \log T$ measured from Be 3130.42 as intensity standard.

remain visible to as low concentrations as usually desired, and vanishes into the background for all practical purposes at about 0.05 per cent. Actually, in the 0.066 per cent standard, the Sb line is visible but too weak for accurate measurement. The standard background, also shown on all other curves, is determined by averaging backgrounds of individual spectra. They are shown as horizontal lines where possible. In using this curve to convert $\Delta \log T$ values from unknown samples to concentration, it is imperative that spectra of the unknown have a closely similar background (also measured in $\Delta \log T$ from the standard Be line), otherwise highly erroneous analytical results are obtained, which increase in magnitude as the lines of elements determined approach the background. Individual $\Delta \log T$ values are plotted as small circles and their average is shown as larger circles. This curve is based on the smaller sample arced, so that the lowest limit of detection is only 0.05 per cent rather than about 0.01, which would be obtained by arcing the larger samples. As the weight of standard arced was approximately 2 mg., the 0.05 per cent Sb that can be just detected represents about 0.001 mg. Sb. This, however, is only from $\frac{1}{10}$ to $\frac{1}{500}$ the sensitivity characteristic of other metals for samples of equal size.

Antimony was detected only in the larger samples of two concentrates arced, and is therefore under 0.01 per cent in most of them, although it was found in one sample up to 0.2 per cent Sb. This antimony presumably is carried by minerals other than ZnS in the concentrates. Some galenas and bismuthinites carry 1 per cent Sb.

Bismuth

The experimental curve for Bi 3067.716 line is linear (permitting reliable quantitative determinations) up to at least 3 per cent Bi (Fig. 6). There is some uncertainty at the low concentration end owing to a

residual line in the iron-rich samples, which causes the curve to flatten out at a value of $\Delta \log T = 0.09$ above the background limit. This apparently is a halation ghost from a neighboring strong Fe line; which, with the equipment used, exactly coincides with the Bi line. Its intensity corresponds to 0.02 per cent Bi, but it is not the characteristic wider line of Bi. If it were not present the limit of detection would lie at 0.01 per cent Bi in the small-sized sample arced. The false sensitivity value indicated by standard curves in such instances is evident and their uncritical use in analyzing unknowns leads to errors of several hundred per cent. Note the spread of individual $\Delta \log T$ values and the necessity of adjusting them to a standard background when spectra at low concentrations with higher (or lower, as in this case) backgrounds are secured than at higher concentrations.

A recognizable Bi line was present in only two ZnS concentrates analyzed which, with the large sample arced, represented a few thousandths of one per cent Bi. Most of them contained still less. This low Bi content of natural ZnS was also reported by Oftedal, who found that Bi in sphalerite-galena ores is confined exclusively to the galena in amounts averaging 0.1 per cent but occasionally reaching 1.0 per cent Bi.

Tin

Curves constructed for the line Sn 2839.989, employing both the large and small samples are reproduced as Fig. 7. The tin line vanishes into the background at 0.0005 per cent Sn for the larger sample (curve *L*). A value six times greater is indicated as the vanishing concentration for the smaller sample, by extrapolating the curve labeled *S* in the figure. The rate of increase of intensity with concentration in the tin line for the larger sample begins to depart from a linear relationship at 0.2 per cent Sn and above this point values from individual spectra exhibit greater spreads. These features frequently are

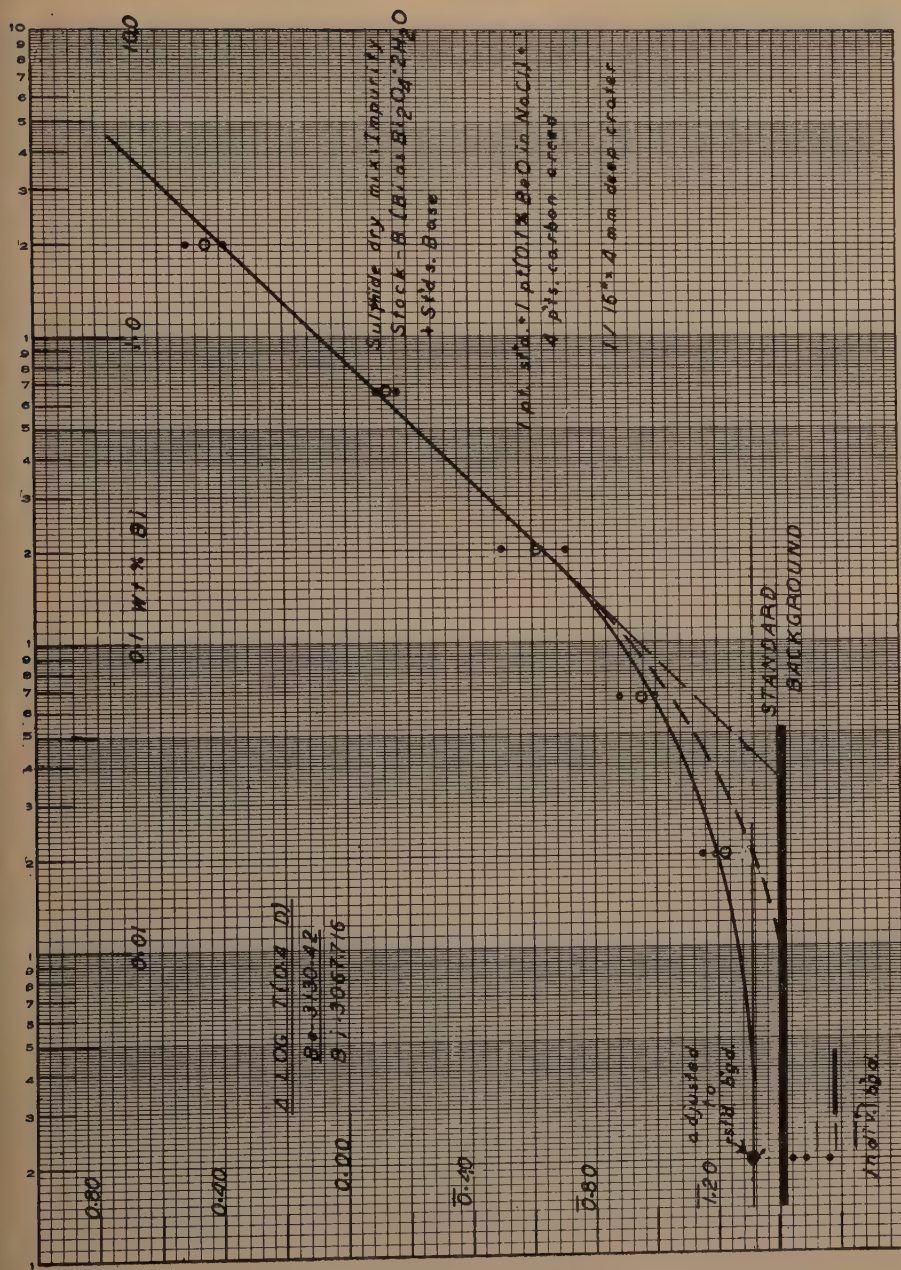


FIG. 6. ---CONCENTRATION CALIBRATION CURVE FOR Bi 366.7-716 LINE IN SYNTHETIC ZnS ORE STANDARDS. Be 3130.42 is intensity standard.

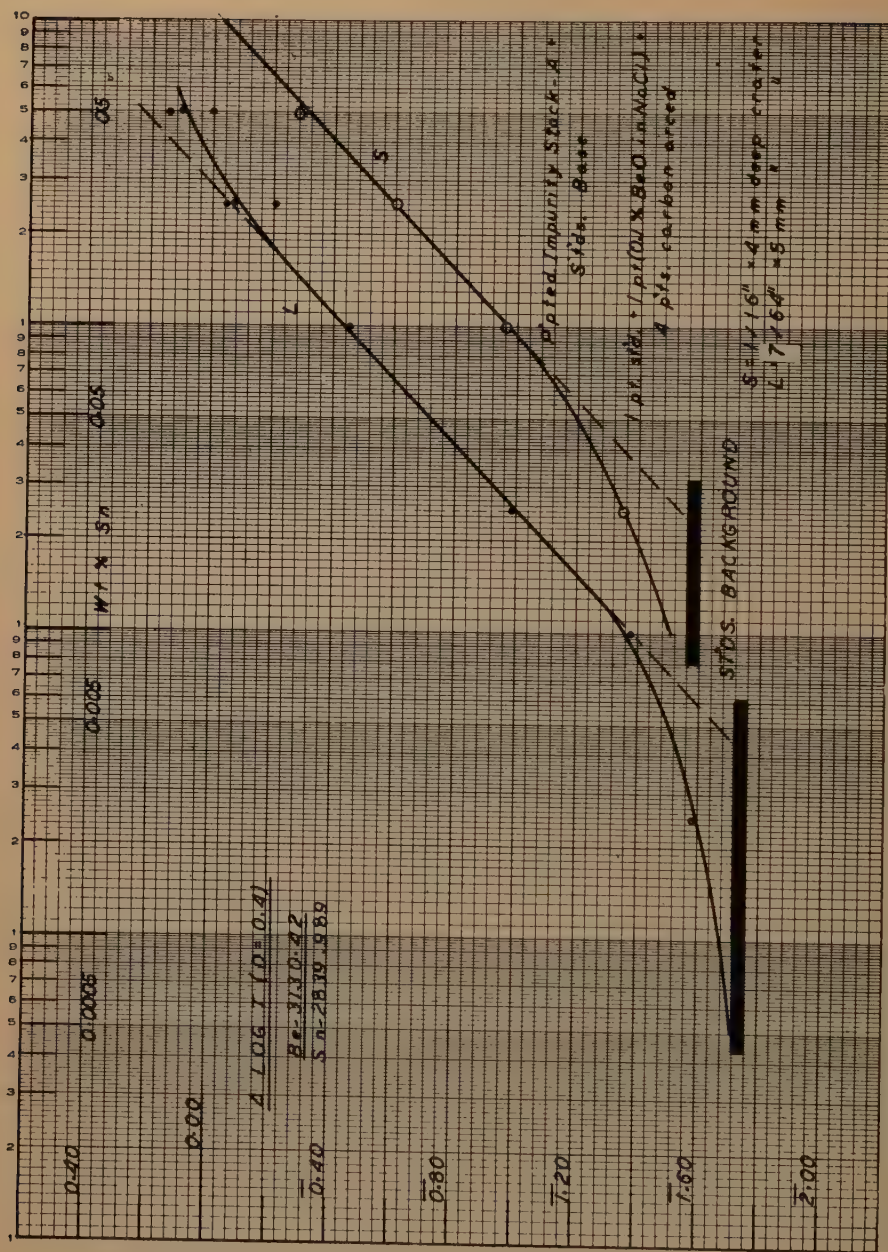


FIG. 7.—CONCENTRATION CALIBRATION CURVE FOR Sn 2839.089 IN SYNTHETIC ZnS STANDARDS USING Be 3130.42 AS INTENSITY STANDARD.

displaced to higher concentration levels of Sn (or other elements) in samples when the minor element is chemically combined with, or contained in, the crystal lattice of an abundant, coarsely crystalline mineral carried by a sample.

The separation of the two curves must be emphasized, as the curves for the large and small samples are similarly separated for all other elements measured. If the intensity ratio of all the impurity lines relative to the standard Be line remained unaltered regardless of sample size, the linear portion of both curves would be superimposed. They would differ only in that the high-concentration end of the large-sample curve would flatten off at a lower concentration than would the small-sample curve; at the low concentration end the small-sample curve would depart from linearity at higher concentration (and at a greater height, measured in $\Delta \log T$, above the background) and vanish more abruptly into the background. The fact that these curves are displaced from each other for all elements involved is proof that *the intensity ratios are not independent of sample size*, and since spectra of ore samples show the same variation, the observed effect is not due to physical differences of ore samples and standards. Since the differences are always in the same direction (but to different amounts) it is apparent that the beryllium line makes the greatest contribution to this shift; in that the line Be 3130 is relatively enhanced in the small-sample spectra, probably because of a decrease in its self-absorption in the thinner arc column. Although this is not a desirable behavior of a line used as intensity standard, the effect could not be eliminated by use of a different internal standard line, since each other element line also contributes some part to the shift in the intensity ratio. This is shown by the fact that the displacement is not equal for all elements involving the same beryllium line in the same spectra. The shift, measured in

$\Delta \log T$, is 0.66 for Pb, 0.54 for Sn, 0.58 for Ga and In, 0.42 for Ag, 0.40 for Cu and 0.17 for Mn. It is beyond the scope of this paper to consider this important matter further, except to warn against the conclusion that a spectrochemical method is rendered foolproof merely by addition of an internal standard.

The amount of tin found in commercial concentrates was around 0.001 per cent in several, from 0.03 to 0.04 per cent in a few and reached a maximum value of 0.15 per cent in one. This represents the maximum content found in any Norwegian galena or sphalerite by Oftedal, who also found a rather sharp temperature dependence for the distribution of tin between these two minerals, in that tin enters ZnS rather than galena at lower temperatures.

Germanium

The experimental curve for germanium (Fig. 8) is based on spectra of small-sized samples of the dry-mixed sulphide standards (series B) for the line Ge-2651.178. No special comment is required except that the lowest limit of detection (0.005 per cent) is higher than expected. That the curve is reliable up to beyond 5 per cent Ge was shown by spectra of the mineral argyrodite ($4\text{Ag}_2\text{S} \cdot \text{GeS}_2$), whose $\Delta \log T$ was ± 0.42 leading to 6.2 per cent Ge—the approximate germanium content of this mineral.

Germanium was found in only one commercial concentrate examined, which contained 0.02 per cent. In all others the amount was under 0.001 per cent. Oftedal also reported the scarcity of Ge in Norwegian sphalerite, and calls attention to the general observation that Ge is enriched only in sphalerites deposited at lowest temperatures—even lower than those rich in gallium.

Gallium

Curves for gallium were constructed for both large and small samples and are

reproduced in Fig. 9 for the line Ga 2943.637. They are separated as shown for tin, and for the same reason. The two corresponding limits of detection are 0.0001 and 0.0006 per cent. The large-sample curve is reliable up to only 0.1 per cent but with the small-size samples 0.5 per cent can be determined. A faint coinciding Fe line is not visible in these spectra. Gallium was found in the concentrates examined in amounts ranging from 0.0005 to over 0.04 per cent, but most frequently in the 0.001 to 0.01 per cent range. Oftedal found Ga ranging from 0.001 to 0.1 per cent in Norwegian sphalerites, with the higher amounts confined to low-temperature deposits. Some analyses made in connection with the work reported herein showed 0.03 per cent Ga in Adirondack (Edwards) sphalerite and 0.12 per cent Ga in pure isolated crystals from Joplin, Mo. No Ga was detected in determinable amounts in pegmatitic sphalerite. I know of no sulphide richer in gallium than germanite, which contains up to 0.8 per cent Ga.

Indium

The lowest limit of detection of indium is about 0.004 per cent for the smaller sized samples used. The curves for indium, reproduced for In 3039.356, Fig. 10, are the same as for gallium except that a weak coinciding Fe line has sufficient intensity to remain visible for these iron-rich samples in spectra from the larger samples arced. The curve for the larger sample (*L*) thus flattens off at a definite height above the background limit—at a $\Delta \log T$ value equivalent to 0.0013 per cent In on the extrapolated blank-free curve, which otherwise would vanish into the background at about 0.00025 per cent In. The determinable limit of detection of In therefore varies with the iron content of the larger sample and is scarcely below 0.001 per cent. An approximate curve for correcting experimental $\Delta \log T$ values for the iron content

of samples being analyzed is shown (inset) in the upper left-hand corner of Fig. 10. According to this curve the iron line is not visible in samples containing under 1.5 per cent Fe—a matter that still requires some additional work.

Indium in concentrates, so far examined, ranges from 0.0005 per cent or lower (determinable only in iron-poor samples) up to 0.2 per cent In. None has been observed in pure Adirondack sphalerite, or in isolated Joplin crystals (therefore under 0.004 per cent In). Oftedal reports a range of under 0.001 up to 0.07 per cent In for Norwegian sphalerites, with a distinct enrichment in those from medium temperature deposits.

Nickel

Curves for both sizes of samples and both sets of standards were constructed for two different nickel lines, the stronger line 3414 (which, unfortunately, lies in a heavy band background) and for a line of the doublet at 3101. The curves for these two lines, using only the smaller samples of dry mixed sulphides, are reproduced in Fig. 11. Nickel can be easily determined in the range 0.005 to 5.0 per cent. Neither line for either set of synthetic standards vanishes into the background but approaches a constant $\Delta \log T$ value equivalent to 0.0045 per cent Ni on a blank-free extrapolated curve. This seems to be a nickel contamination in the standards base used (perhaps in the high-purity ZnS), although this has not been determined with certainty, since many ore samples show a similar line, which may be an air line in the spectra. Extrapolated blank-free curves vanish into background at 0.002 to 0.003 per cent Ni for small samples. Nickel, if present, in all ore samples examined, is not more than 0.005 per cent and probably is much less. The individual and average backgrounds for each standard are indicated in the figure.

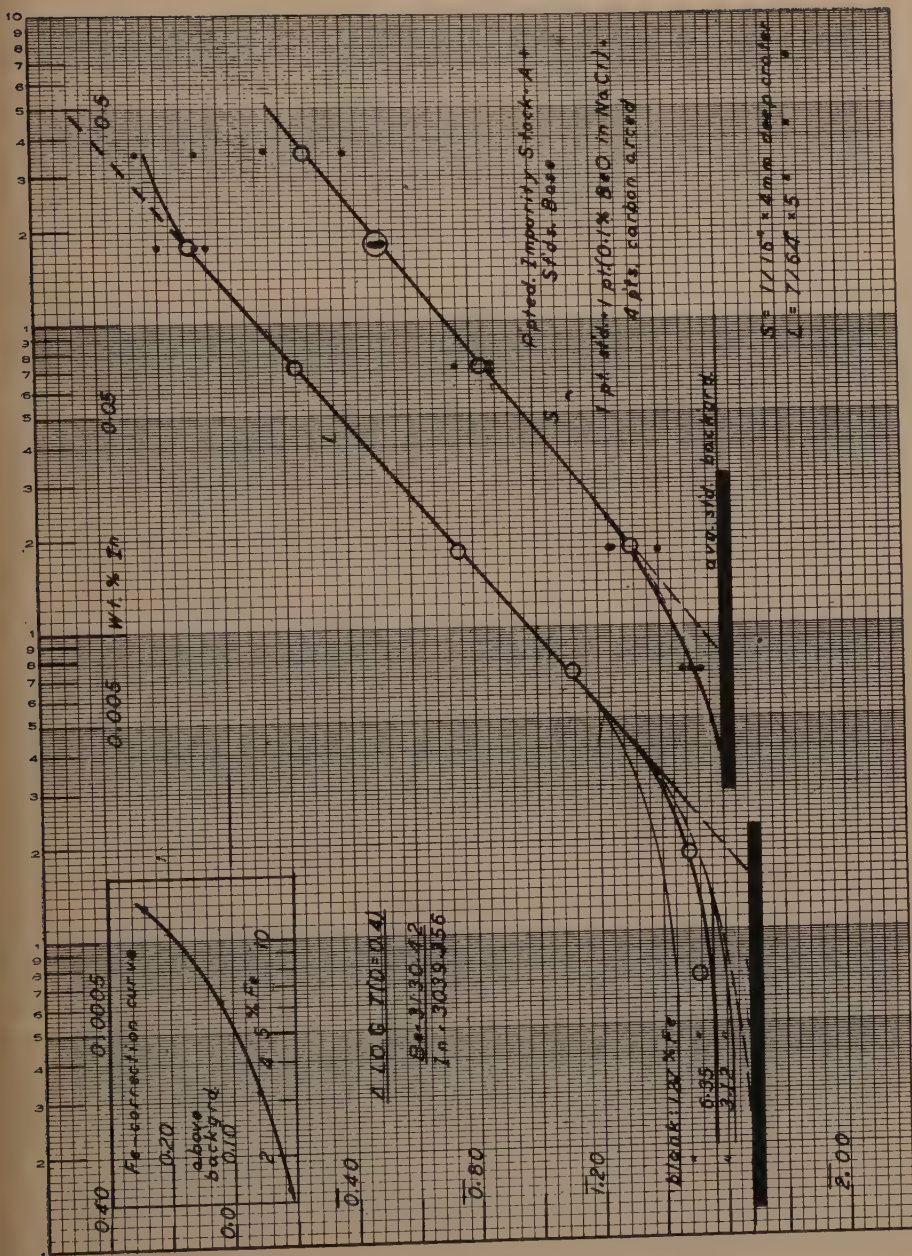


FIG. 10.—CONCENTRATION CALIBRATION CURVE FOR IN 3039.356 IN SYNTHETIC ZnS STANDARDS USING Be $^{3130.42}$ AS INTENSITY STANDARD.

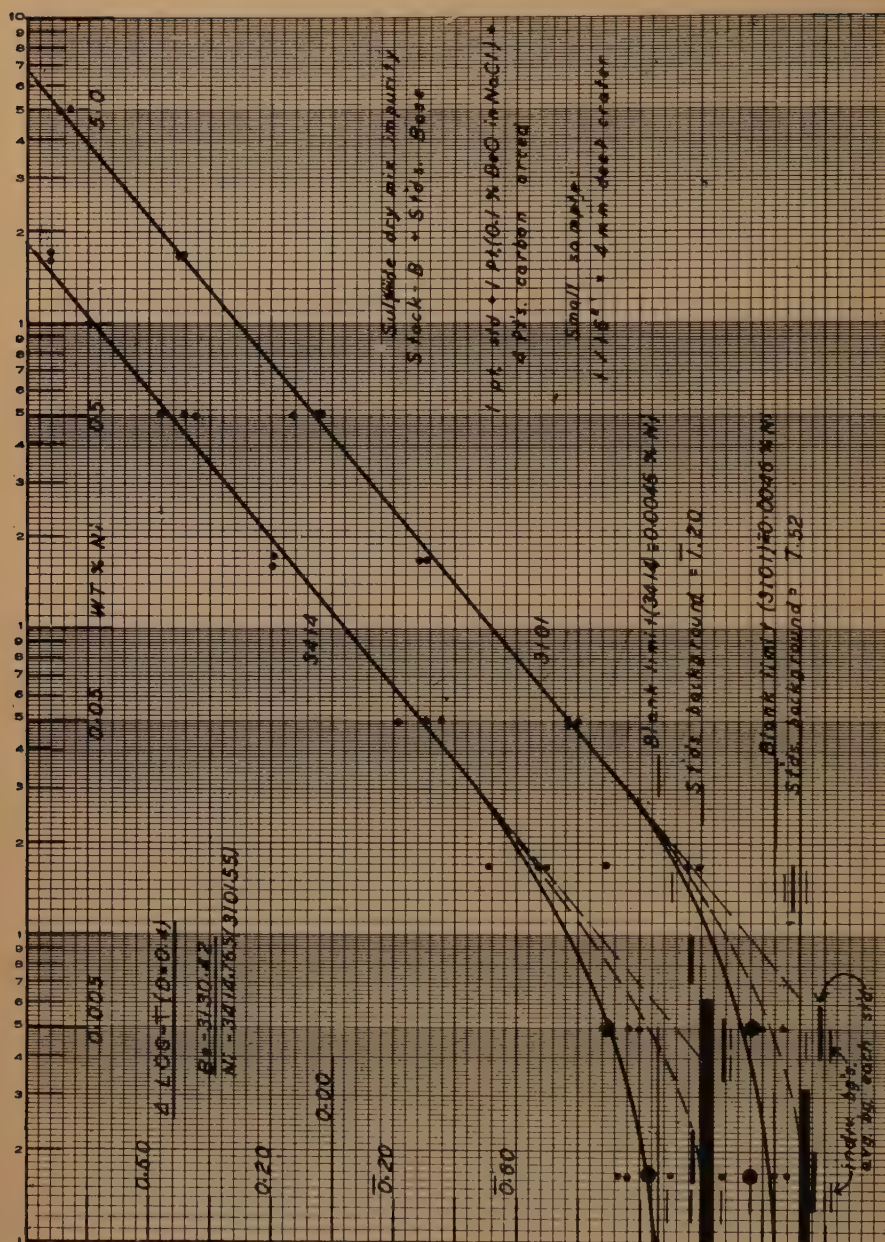


FIG. 11.—CONCENTRATION CALIBRATION CURVES FOR Ni 3414.76 AND Ni 3101.55 LINES IN SYNTHETIC ZnS STANDARDS USING Be 3130.42 LINE AS INTENSITY STANDARD.

Cobalt

The curves for two cobalt lines, 3453.605 and 2536.493 Å., are shown in Fig. 12, both based on small samples of dry-mixed sulphide standards. Although the background at the longer wave-length line is very dense, owing to CN-band spectra, there is no difficulty with a residual line as observed for Ni. Quantitative determinations from 0.002 to 2 per cent Co are possible with the line Co 3453, and from 0.5 to 10 per cent Co with the 2536 line. The latter coincides with the strongest Hg line, so that by this method traces of Hg cannot be detected in samples containing more than 0.2 per cent Co. Cobalt is present in many concentrates in amounts up to 0.02 per cent, but in most it falls in the 0.001 to 0.01 per cent range. Pure Adirondack sphalerite was found to contain 0.02 per cent Co but none (under 0.002 per cent) was detected in isolated crystals from Joplin, Mo. These results are in line with Oftedal's results on Norwegian sphalerites except that he found up to 0.2 per cent in those of high-temperature origin.

Thallium and Mercury

The remaining two elements in the "spectrographic group" are thallium and mercury, whose experimental concentration calibration curves are not reproduced for this paper. Thallium cannot be determined to very low concentrations by this method. The lowest limit of detection with the method used is about 0.01 per cent and any thallium present in the concentrates so far examined is less than this amount. However, it is known that thallium is occasionally present in amounts up to 0.05 per cent in some galenas.

Standards for mercury cannot carry more than 0.2 per cent Co, so that usable spectra were not obtained from either series of standards employed in this work. Since mercury was detected in only one sample examined, it did not seem necessary to

prepare an entire new series of standards for determining mercury alone at this time. The limit of detection of mercury for the method used is known to be about 0.01 per cent, for the Hg line 2536 was clearly visible in a sphalerite from Spitzbergen, known to contain 0.025 per cent Hg.

SPEED AND EXTENSION OF THE METHOD FOR DETERMINING THE MORE ABUNDANT METALLIC CONSTITUENTS IN ZnS

No particular emphasis was placed on speed in the experimental work reported herein, but in any attempt to apply quantitative spectrographic methods to the routine analysis of ZnS ores in industry, the question of time naturally arises.

Considerable progress has already been made in determining by the spectrographic method described those other more abundant minor metallic constituents of ZnS ores that normally are determined by standard chemical methods (namely Ag, Cu, Cd, Pb, As, Mn, and Fe). The results of this additional work will be published when completed. Then 16 different metals can be simultaneously determined in ZnS concentrates, over a total concentration range of 1:100,000 (namely, from 0.0001 to 10 per cent) for the several elements present. This will provide duplicate assays for all elements, four individual checks for many and six for a few. The total time required for one trained operator, set up for routine work, to turn out final results for all these elements in one sample will be a minimum of three, and a maximum of four, hours. This includes the preparation of a small spectrographic sample from one of 100 to 200 mesh of the usual size for chemical assay. Three different samples can be analyzed in duplicate, in the same time, when spectrographic determinations are not desired for those elements present either in greatest abundance or in faintest traces. It should be recalled that samples

as small as 10 to 50 mg. can be analyzed in the same manner, which is of great value in geochemical and ore-dressing investigations.

Extension of the method to Ag, Cu, Cd, Pb, As, Mn, and Fe awaits only more critical joint chemical and spectrographic assays on identical samples and recheck of spectrographic curves with new standards containing the elements in coarser crystalline natural sulphides.

In conclusion, it should be pointed out that from a geochemical viewpoint indium is the only metal that occurs as a minor constituent in sphalerite, which occasionally accompanies zinc in this mineral in amounts equivalent to their original ratio in average silicate rocks (namely $\text{Zn}:\text{In} = 400:1$, equivalent to 0.15 per cent In in ZnS). All other metals are greatly depleted relative to Zn in natural ZnS, even those which, at some localities, constitute an unusually abundant characteristic minor constituent of the zinc sulphide ore. It is planned to present a later paper on the geochemistry of ZnS ores and minerals, which will treat more fully the distribution of minor metals in these ores and make extensive use of the quantitative

spectrographic procedure described as the primary purpose of the present paper, as well as to utilize published results of others on the minor constituents of natural ZnS minerals.

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Spectrographic Analysis of Special High-grade Zinc

By A. Y. BETHUNE,* MEMBER A.I.M.E., AND W. W. SCHMITTROTH*

(Chicago Meeting, February 1946)

THE commercial analysis of Special High-Grade zinc usually involves the determination of lead, iron, copper and cadmium as impurities in the base metal. Over the past 20 years, as the result of metallurgical improvements in the art of producing Special High-Grade zinc metal there has taken place a gradual exclusion of almost all extraneous elements, and the few that do remain in the final product have been virtually reduced to the vanishing point. Thousands of tons of zinc are now commercially produced annually and made available to the trade, in which impurities are present only in the order of 0.0010 per cent or less and the sum total of all impurities does not exceed 0.0025 per cent. To such zinc the term "super-purity" might well be applied without undue exaggeration.

The techniques used for production control and final analysis of Special High-Grade zinc by means of emission spectra in the laboratories of the electrolytic zinc plant of the Sullivan Mining Co. are based on the premise that self-electrodes are to be preferred over all other forms for the examination of the zinc in question. Furthermore, after a survey of the literature and considerable experimental work,¹ it was decided that the spectrographic method of internal control, the principle of which was first announced by Gerlach,² using a modification of the high-voltage alternating-current

arc source introduced by Duffendack and Thompson,³ with the calibration of each photographic plate as recommended by Wolfe,⁴ would yield the most accurate and reproducible results.

Self-electrodes were chosen in order to make use of one of the unique advantages inherent in spectrographic analysis; namely, the rapid and almost effortless detection of elements other than those being quantified by the analyst; or conversely, the proof that the zinc is free from such impurities if no spectral line of the suspected element appears. This fact was verified for certain elements, and will be discussed later.

Carbon electrodes impregnated or packed with zinc salts chemically prepared from the zinc to be assayed were avoided for a number of reasons. First, the chemical manipulation was another time-consuming step, which increased the chances for contamination. Second, none of the common zinc salts, such as the chloride, nitrate or sulphate, yielded reproducible results under our conditions, nor did the spectral line of the impurity appear as readily in the low concentrations as when using zinc metal. Third, no commercial carbon, except the very expensive, was pure enough to use with this grade of zinc and the continued time, effort and expense incurred in the purification of carbon were not desirable.

The use of Special High-Grade zinc self-electrodes introduces certain complications with regard to obtaining satisfactory excitation conditions, because it seems necessary to raise the temperature

Manuscript received at the office of the Institute Jan. 12, 1946. Issued as TP 2066 in METALS TECHNOLOGY, September 1946.

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¹ References are at the end of the paper.

characteristics of the secondary. For this work the setting remains constant, as determined by experiment. A 25-kva. pole-type outdoor-service transformer is

The analytical gap is enclosed in a wire-screen cage, provided with a safety switch activated by the door through which the operator must work. The safety switch

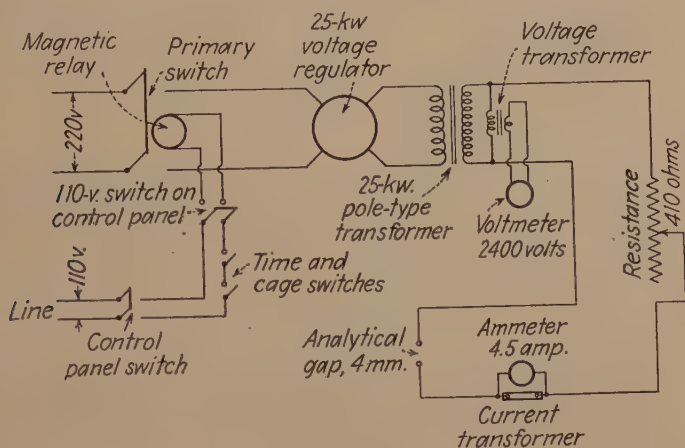


FIG. 3.—CIRCUIT DIAGRAM.

used in order to have sufficient capacity to deal with other problems should the need arise.

The secondary consists of two banks of resistance wire loosely wound on Transite board, in series with the analytical gap. The total resistance used is 410 ohms. The wires attain a red heat during operation. This arrangement is not ideal because resistivity of wire changes with temperature. However as each exposure is identical in time, electrical conditions are very similar from one exposure to the next, and results are reproducible. Perhaps a better plan would be to have "Copel" wire of sufficient carrying capacity to keep from showing any color for the duration of an exposure. A voltage transformer and a current transformer are connected to meters in the secondary circuit, as shown.

The source is controlled by automatic timing switches connected to the 230-volt supply to the primary. They allow time intervals from one second to fourteen minutes.

is in series with the timers and the whole cage is grounded. The arc stand and electrode holders are patterned after those used by Duffendack and Wolfe,⁶ and described in their paper on the analysis of caustic liquor.

The spectrograph used in this work is one of the large automatic type, with the Littrow prism mounting, manufactured by Adam Hilger of London. It has both the glass and quartz optics but only the quartz optics are used in this case.

In most spectrographic analyses, the spectrographer has a number of lines from which to choose and makes his line selection according to the dictates of theory and experiment. In this work the spectrographer has very little choice and must adjust his conditions to make best use of the lines at his disposal.

For example, if we consider the spectral range from 5000Å. to 2100Å., only two lines of copper appear in the spectrum of Special High-Grade zinc electrodes when the copper content is between 0.001 and 0.00001 per cent. Cadmium produces only

one line between 0.0004 and 0.00001 per cent and two lines between 0.001 and 0.0004 per cent. Lead has four useful lines between 0.002 and 0.0001 per cent.

and it is recognized that the most suitable line would be one having very nearly the same wave length as the line used for the analysis element. The proximity in wave

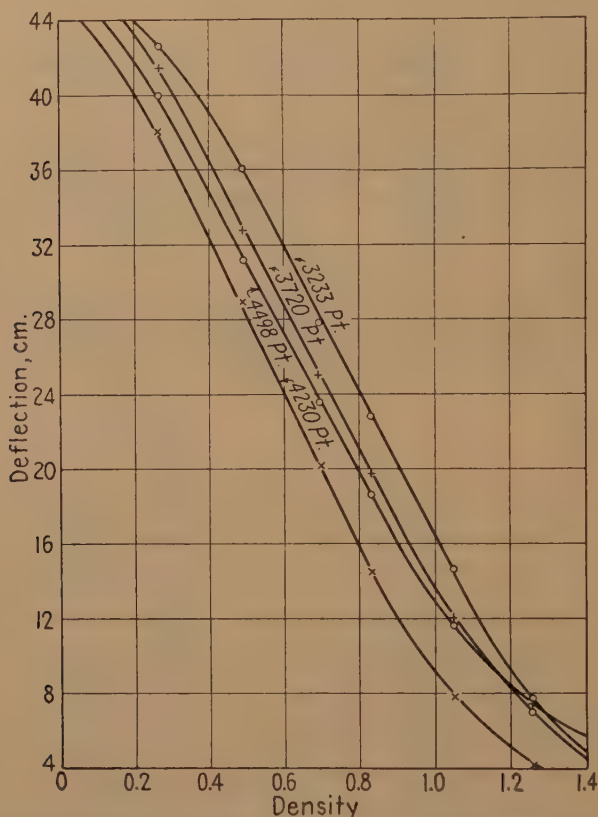


FIG. 4.—HILGER STEP FILTER. PLATE GAMMA, EASTMAN 103-0, REGION 5000 TO 2810 Å.

Although iron has several lines between 0.002 and 0.0005 per cent, there is only one useful line below 0.0005 per cent.

The method of internal control demands some line in the same spectrum, which responds to light source fluctuations in the same way as the line of the analysis element, and to which the analysis element may be referred. The two lines must exhibit a similar variation in spectral intensity when random fluctuations in the source cause changes of excitation conditions.

For self-electrodes the reference line usually is chosen from the matrix element,

length avoids variation in plate contrast and proximity on the plate minimizes errors due to variation in emulsion sensitivity from point to point.⁷ The zinc spectrum being relatively "simple" makes it difficult for the spectrographer to choose reference lines for internal control that meet these conditions. If sufficient current is used to excite the atoms of elements present as minutiae in the matrix, then all but a few of the zinc lines will appear overexposed.

Of the remaining zinc lines in the 5000° to 2800 Å region, which permit photometering only 4292 Å and the 4629 Å

seem to respond to source fluctuations as do impurity lines. However these lines have proved satisfactory for internal control when Eastman 103-0 plates are used, running at least one standard, and frequently two, on every plate. Fig. 4 shows the gamma of these plates in the regions used for the analytical lines. The slopes are so nearly parallel that little error is introduced by using zinc reference lines that are rather far removed from the lines of the elements to be assayed. Line 2530\AA , Zn is used with line 2288\AA Cd because of its intensity when using the time of exposure necessary to bring out the Cd line when Cd is present in the range of 0.0001 to 0.0005 per cent. It is recognized that because of its asymmetrical nature¹⁰ the 2530\AA Zn is not an ideal line for control purposes. However, as mentioned earlier, a limited choice of lines dictated the use of this one, and continued application has shown it to be acceptable. Other zinc lines in that region are either overexposed or highly diffuse.

The 2357\AA Pt line is used to calibrate the plate. Although all three lines (2530\AA Zn, 2357\AA Pt, 2288\AA Cd) vary in gamma, experience has proved that they are sufficiently parallel to give reproducible results when analyzing cadmium in the 0.0001 per cent to 0.0005 per cent range.

The photographic plates are calibrated by using the analytical source between platinum electrodes making the exposure through a rhodium-coated step-filter, then photometering selected platinum lines. The platinum electrodes are made by drilling a hole in $\frac{1}{4}$ -in.-diameter pure carbon electrodes, inserting a 1-in. length of heavy platinum wire therein, and burning them in the analytical source until the tips melt into a globule. When in globular form, the consumption of platinum is negligible and the electrodes do not become oxidized. The technique for analysis is as follows:

PREPARATION OF ELECTRODES

The samples of plant production of zinc metal are delivered to the laboratory in the form of small "fingers" poured in the melting and casting department as the lots are being produced. The zinc metal baths of the melting furnaces are sampled by dipping with ordinary clay crucibles such as are used for fire assaying and the crucibles with their solidified metal contents are delivered to the laboratory. In either case the zinc samples are transferred to a Dixon No. 6 graphite crucible and remelted by a gas-fired furnace. Very little dross is formed during the remelting of the sample fingers from the regular plant even when no drossing agent is used. When irregular shapes are melted, such as zinc cathode sheet, the addition of 5 to 10 grams of C. P. granular ammonium chloride reduces the quantity of dross, which ordinarily results from melting this form of zinc in air, to a relatively small amount. In either case analyses of the dross show no enrichment of the impurities as compared with the original sample, and no evidence was found that the concentration of impurities in the original sample was changed because of drossing.

The molten zinc is stirred with a carbon rod, then poured into graphite molds to form the electrodes. Fig. 5 shows the zinc being poured into the graphite mold in the iron stand, which also serves to center the 12 by $\frac{1}{4}$ -in. carbon rod. The carbon rods are cut off $1\frac{1}{4}$ in. above the zinc with electrician's wire-cutting pliers and the electrodes are placed with tips pointing upward in a wooden tray, drilled with $\frac{5}{16}$ -in. holes. A draft from an electric fan hastens cooling. The zinc electrodes do not require machining or mechanical preparation in any way. The shape of the tip is suitable as cast.

It was determined by experiment that errors due to "salting" with zinc dross or zinciferous dust could occur if particles found their way into the bottom of the

mold and thence onto the tip of the electrodes. This possibility is circumvented by cleaning the tips in a 10 per cent (by volume) hydrochloric acid solution at

checked spectrographically. No trouble is experienced in obtaining homogeneous lots. Usually two sets of electrodes are maintained so that standards are available



FIG. 5.—ZINC BEING POURED INTO GRAPHITE MOLD IN IRON STAND.

room temperature. The tips are first immersed in the weak acid for 3 min., washed with distilled water and dried with a paper towel. It should be mentioned that this surface cleaning does not affect the validity of the assay by causing low results. The acid bath removes about 5 mg. of zinc per square inch of surface immersed. Invariably, a high iron or lead content of the metal will be detected and quantified. Approximately 250 mg. of zinc is consumed during an exposure of 120 sec. Fig. 6 shows the electrodes in place in the arc stand.

Several hundred electrodes for use as "standards" are cast from one lot of zinc and are used day by day as needed. The lot is carefully analyzed chemically for lead, iron, copper and cadmium and

for lead, iron and copper in range of 0.001 to 0.005 per cent and 0.0001 to 0.0009 per cent. The cadmium in both sets of standards is usually in the range of 0.00005 to 0.0001 per cent.

The standard electrodes are treated in the same manner as the samples to be analyzed. Samples usually are run in duplicate; sometimes in triplicate; that is, either two or three sets of electrodes are cast and the results averaged to give the reported assay.

EXPOSURES

The time of exposure for the lead and iron determination is 120 sec. with no preburn. The electrodes are adjusted as to height and spacing with a gauge lens, the door of the cage is closed and the exposure

started by releasing the automatic timing switch. The arc is first struck with the analytical gap set at 2 mm.; this is immediately opened to 4 mm. and kept there for

The spectral region used for the copper, lead and iron assays is 5000 to 2810 Å. If the cadmium is 0.0005 per cent or higher it may be detected and quantified

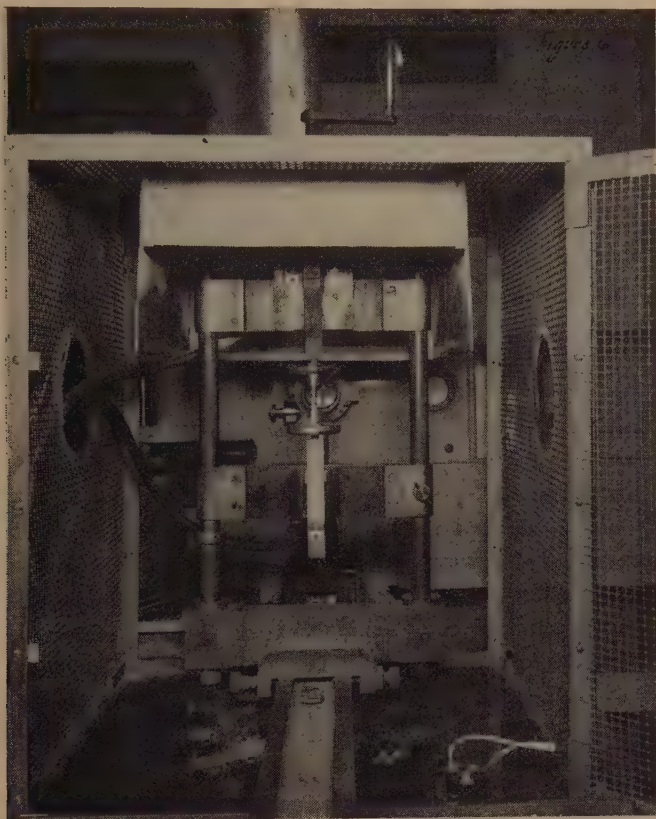


FIG. 6.—ELECTRODES IN PLACE IN ARC STAND.

the remainder of the exposure. One spectrogram serves to obtain both the lead and iron. If iron is below 0.0002 per cent no line will appear in an exposure of 120 sec. A longer exposure is necessary to bring out iron of lower concentrations.

The copper determination is made on a new spectrogram, using the same electrodes as were used for the lead and iron. These electrodes now have a preburn of 120 sec. The exposure is for 60 sec., made through a rotating interrupter set to cut out three fourths of the light.

by using the same spectrogram as that from which the lead and iron were determined.

If the cadmium is below 0.0005 per cent fresh electrodes must be used and the spectrograph shifted to the 2850 to 2200 Å region. The exposure is for 120 sec. with no preburn and no interrupter.

For plate calibration platinum electrodes are arced for 10 sec.

All exposures are made with the source of light 38 cm. from the slit of the spectrograph, which is set at an opening of 0.025 mm. A spherical condensing lens (Hilger

1025) is placed 2 cm. in front of the slit and focused on the collimating lens.

The exposed photographic plates are developed for $1\frac{1}{2}$ min. with Eastman

plate is used to measure the density of the spectral lines. Spectrograms usually are taken at a 3-mm. width for certified assays, but on some control and experi-

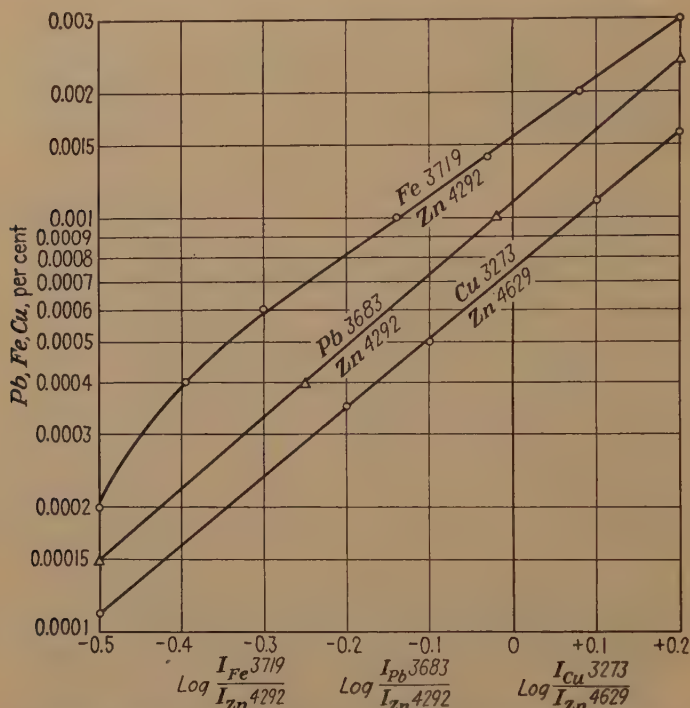


FIG. 7.—WORKING CURVES, LEAD, IRON AND COPPER IMPURITIES IN ZINC METAL. MASSIVE ELECTRODES, 175 GRAMS.

D-19 at 18°C. in an ARL-Dietert constant-temperature developing machine, transferred to the second tray for a 20-sec. shortstop in dilute acetic acid (35 ml. glacial acetic acid in 1000 ml. water), and then fixed for 4 min. in Eastman concentrated X-ray fixer. The plate is washed for 5 min. in filtered domestic water, sponged, washed with distilled water and dried. The drying is accomplished by placing the plate over a heating element, emulsion side up, and blowing an air blast over the surface.⁸

MICROPHOTOMETRY

A Hilger nonrecording microphotometer accommodating a 4 by 10-in. photographic

mental work good results have been obtained with a 2-mm. width. Table 1 shows the lines used and their ranges.

TABLE 1.—Spectral Lines¹⁰

Element	Wave Length, Å.	Range of Concentration, Per Cent	Reference Line of Zinc
Pb	4057.82	0.0001 or lower	4292.89
Pb	3683.47	0.004–0.0002	4292.89
Pb	3639.58	0.004 or higher	4292.89
Pb	2843.07	0.005–0.0005	4292.89
Fe	3719.94	0.01–0.0015	4292.89
Fe	3273.13	0.01–0.001	4292.89
Cu	3273.96	0.002–0.0001	4629.81
Cu	3247.54	0.002–0.0001	4629.81
Cd	3261.06	0.01–0.0005	4292.89
Cd	2288.02	0.0005 or lower	2530.09

Working curves were first drawn by using standard zinc electrodes with im-

purity values established by chemical analysis. To minimize errors due to source fluctuations beyond the control of the spectrographer, either one or two stand-

the element is in the range of 0.0001 to 0.0009 per cent. For example, a true 0.0005 per cent Pb might be reported as 0.0004 per cent or 0.0006 per cent.

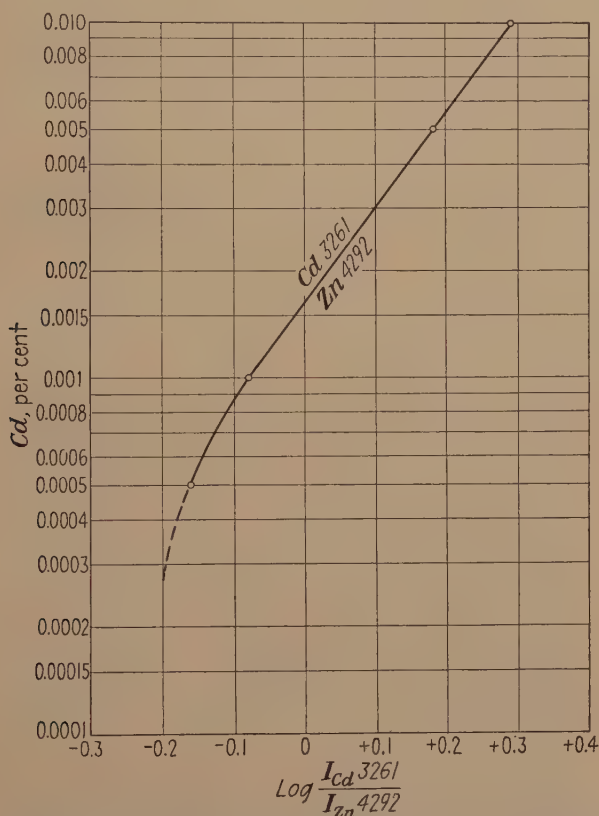


FIG. 8.—WORKING CURVE, CADMIUM IMPURITIES IN ZINC METAL, HIGH VALUES. MASSIVE ELECTRODES, 175 GRAMS.

ards are run on every plate. This precaution tends to correct any deviation of the assay from the true value caused by a slight shifting of the working curve. Figs. 7, 8, and 9 show typical working curves for lead, iron, copper and cadmium.

The final proof of the accuracy of the method was established by daily comparison with accurate chemical analyses on the same samples. The method can be relied upon to yield results within ± 10 per cent of the amount of impurity present if the element is in the range of 0.001 per cent to 0.009 per cent, or 20 per cent if

This compares very favorably with the limits of accuracy of well-tested chemical methods in the same ranges.

Table 2 shows some comparisons of chemical and spectrographic results. The chemical samples were prepared from the same melt but by a different method than was used for the massive spectrographic electrodes. The chemical samples were converted to "mossy" zinc in accordance with a standard practice of long duration. The comparison, therefore, represents the results obtained by independent sampling of the same material.

TABLE 2.—*Chemical and Spectrographic Results*

Sample No.	Pb, Per Cent		Fe, Per Cent		Cu, Per Cent		Cd, Per Cent	
	Chemical	Spectrographic	Chemical	Spectrographic	Chemical	Spectrographic	Chemical	Spectrographic
A	0.0006	0.0007	0.0005	0.0005	0.0005	0.0006	0.0001	0.0001
B	0.0007	0.0007	0.0013	0.0014	0.0006	0.0006	0.0001	0.0001
C	0.0008	0.0009	0.0008	0.0008	0.0005	0.0006	0.0001	0.0001
D	0.0006	0.0006	0.0010	0.0010	0.0007	0.0007	0.0001	0.0001
E	0.0008	0.0008	0.0012	0.0012	0.0006	0.0006	0.0001	0.0001
F	0.0012	0.0012	0.0015	0.0013	0.0008	0.0007	0.0001	0.0001
G	0.0010	0.0010	0.0007	0.0007	0.0007	0.0006	0.0001	0.0001
H	0.0008	0.0008	0.0007	0.0007	0.0020	0.0020	0.0001	0.0001
K	0.0010	0.0009	0.0006	0.0007	0.0012	0.0012	0.0001	0.0001
L	0.0006	0.0005	0.0007	0.0006	0.0005	0.0006	0.0001	0.0001
M	0.0005	0.0005	0.0006	0.0005	0.0005	0.0005	0.0001	0.0001
N	0.0005	0.0004	0.0005	0.0005	0.0005	0.0007	0.0001	0.0001

The time required for one man to prepare, analyze and report results on four metal samples for the four elements is

including appropriate standards and calibration spectra. Twenty spectra of 3-mm. width plus one calibration spectrum of

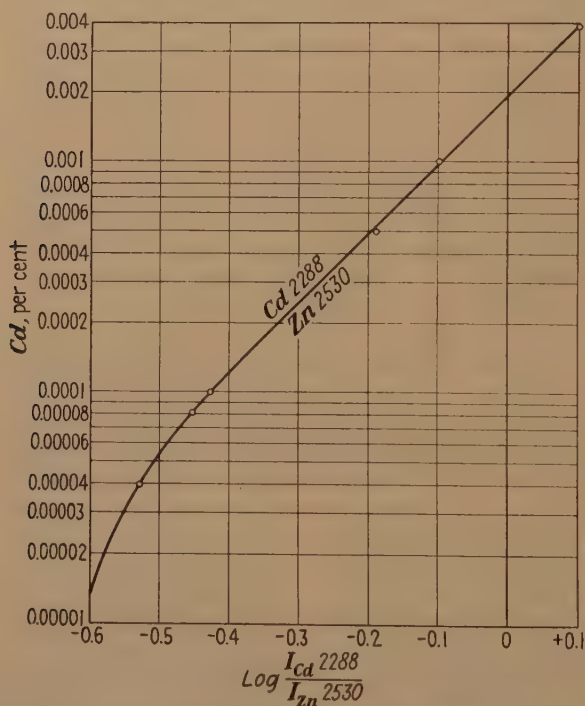


FIG. 9.—WORKING CURVE, CADMIUM IMPURITIES IN ZINC METAL, LOW VALUES. MASSIVE ELECTRODES, 175 GRAMS.

about $3\frac{1}{2}$ hr. This includes melting the delivered samples, casting eight electrodes per sample, running two plates, with each determination in duplicate,

10-mm. width will fit nicely on a 4 by 10-in. plate. One plate in the 5000 to 2810Å region is used for the lead, iron and copper assays plus four standards; two

for lead and iron, two for copper. The other plate, on the 2850 to 2200Å region is used for eight spectra of cadmium plus two standards.

A study was made on the detection of certain elements other than the four usually quantified in Special High-Grade zinc, to prove that very small concentrations would be revealed under these spectrographic conditions employed for quantitative analysis. Sawyer has pointed out that the absence of a spectral line does not permit the conclusion that the element is absent from the emitting source. The absence of the detection lines of an element indicates that it is not present in the sample in sufficient amount to be detected with the source used.⁹

A master alloy was made containing 0.08 per cent Sn, 0.09 Bi and 0.03 per cent Al, remainder Special High-Grade zinc, which was chemically tested and found free from these elements. The alloy was checked chemically. This was diluted with 999 parts Special High-Grade zinc, cast into electrodes and a regular 120-sec. exposure was made. Both the 3175ÅSn (0.00009 per cent) and the 3067ÅBi (0.00008 per cent) appeared but the 3961ÅAl (0.00003 per cent) did not. A new alloy containing aluminum (0.0001 per cent) was made and the 3961ÅAl line appeared. These procedures were repeated, and from the results obtained it has been concluded that if neither the 3175ÅSn line, the 3067ÅBi line nor the 3961ÅAl line appear in the spectrogram taken for the lead and iron determinations, the individual concentrations of tin, bismuth and aluminum are below 0.0001 per cent.

CONCLUSIONS

A spectrographic method for the examination and quantitative analysis of Special High-Grade zinc, using self-electrodes requiring the minimum of prepara-

tion, has been developed. Through daily plant operation and constant checking with reliable chemical methods, it has been proved to be satisfactory for the production control and final analysis of very high-purity zinc metal. By varying the details of the method, it can be applied to lower grades of zinc in which the impurities considered herein are present in higher orders. Also, it may be applied to the detection and quantification of other elements in zinc, should occasion require.

ACKNOWLEDGMENTS

This spectrographic laboratory is fortunate in having at its disposal a complete chemical laboratory staffed by competent analysts who have had long experience working with Special High-Grade zinc. Mr. Leo Baumeister has developed special chemical methods particularly adapted for use on superpurity zinc metal and to him go our thanks for the many check analyses performed and constructive criticism offered in this work. Thanks are due also to Mr. W. G. Woolf, Superintendent of Sullivan Mining Company's electrolytic zinc plant, for encouragement in this project; to Dr. R. A. Wolfe, Research Physicist of the University of Michigan, and to Dr. O. S. Duffendack, Director of Research, The North American Phillips Co., for helpful suggestions and advice, and to Mr. O. J. Jasberg, Design Engineer, Sullivan Mining Co., for drawings used in this paper.

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The Determination of Oxide Cobalt

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(New York Meeting, March 1947)

A METHOD for the chemical differentiation of oxidized cobalt from sulphide cobalt in complex mine and concentrator products is of considerable interest to a number of mining companies throughout the world. At Rhokana Corporation, in Northern Rhodesia, for instance, cobalt is found chiefly in the sulphide form, as carrollite, but a cobalt oxide mineral also occurs irregularly underground, and relatively small quantities in the mill feed from time to time are difficult to detect visually at the concentrator. The oxide cobalt is not amenable to the sulphide flotation process used at Rhokana and nearly all of it passes into the tailing. The occasional period when high tailing losses occur with no appreciable change in the cobalt content of the mill feed has naturally been disturbing to the concentrator staff, who had no means of determining whether an influx of cobalt oxide ore or laxity on the part of the mill flotation operators was responsible for these results.

A procedure for determining oxidized copper minerals, based on their solubility in dilute sulphuric acid saturated with SO_2 , has been used for many years in the copper industry. In the presence of cuprite the procedure fails, but otherwise it gives results quite satisfactory for control pur-

poses. Empirical methods for determining oxidized forms of zinc and lead have been proposed, but they are generally unsatisfactory except in isolated cases of a very simple ore. No published procedure for determining oxidized forms of cobalt or similar elements has come to the authors' notice.

EXPERIMENTAL PROCEDURE

There are obviously two alternatives in attacking a problem of this nature. One is to employ a solvent for oxide cobalt that will not dissolve cobalt sulphide. The other is to find a substance capable of oxidizing the cobalt sulphide to sulphate, which of course is water-soluble and can then be leached from the water-insoluble oxide cobalt.

A representative sample of Rhokana cobalt oxide ore was secured, ground to minus 200-mesh, and carefully rolled to furnish a standard sample for this work. The analysis of this material gave the following percentages: Co, 0.55; Cu, 1.64; Fe, 2.98; S, 0.08; SiO_2 , 41.42; Al_2O_3 , 11.20; CaO, 13.82; MgO, 3.80. As a source of cobalt sulphide a similar large sample of carrollite was prepared, analyzing Co, 23.36 per cent; Cu, 27.32; and S, 31.13. This sample of course was not pure carrollite, but was the best obtainable in quantities sufficient for a standard intended for considerable work. It was a pure sulphide sample, microscopic examination showing only carrollite, a little bornite, and gangue, with no visible sign of oxidized ore present.

A wide variety of reagents as used in an effort to selectively dissolve oxide cobalt or to oxidize sulphide cobalt to

Manuscript received at the office of the Institute Aug. 27, 1945; revised June 5, 1946. Issued as TP 2050 in METALS TECHNOLOGY, September 1946.

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sulphate without affecting the oxide mineral. A ratio of 100 ml. of leach solution to 2 grams of cobalt oxide ore was used throughout this work. The following reagents were used: dilute acids, alkalies, ammonia, and neutral salts, alone and in the presence of oxidizing agents like H_2O_2 , $(\text{NH}_4)_2\text{S}_2\text{O}_8$, KMnO_4 , etc. Various periods of contact and temperatures were also employed. None of these as successful; a solvent strong enough to dissolve all the oxide cobalt attacked the sulphide to an appreciable extent, and conversely any oxidizing agent strong enough to change the cobalt sulphide to sulphate also dissolved the oxide cobalt.

At this stage we secured the kind cooperation of the laboratories of Union Minière du Haut Katanga in the neighboring Belgian Congo. Up to the present the rich cobalt ores of this company have been almost exclusively oxide. The results obtained by Union Minière on its ores indicated that the latter were nearly completely soluble in many of the reagents, like dilute acids saturated with SO_2 , which we had previously tried on Rhokana ores with no success. We repeated our work, varying the time of contact, agitation, temperature, etc., and corroborated our original results.

This pointed to a marked difference in the composition of the cobalt oxide ores of Nkana and Katanga. Since the Rhokana oxide cobalt was apparently much more refractory toward dilute acid solutions saturated with a reducing agent than the Congo ores, we reasoned that this must be due to the occurrence of cobalt in our oxides as a silicate or a refractory oxide, or in very intimate association with silicate minerals. In any case the addition of a little hydrofluoric acid to the solvent should theoretically give complete, or nearly complete, extraction of the oxide cobalt.

We did not know the solvent effect of hydrofluoric acid on sulphide cobalt,

but were hopeful that in the presence of a reducing agent like SO_2 its effect on carrollite would be small. Our experience with oxide copper ores indicated that the solution of sulphuric and sulphurous acids used to leach these minerals dissolved only very small quantities of the copper in carrollite.

The results of a further series of leaching tests, employing hydrofluoric acid, provided the following information:

1. Cobalt can be completely extracted in 3 hr. from Nkana cobalt oxide ore by the addition of HF to a 5 per cent H_2SO_4 , or 10 per cent HCl solution, saturated with SO_2 . The best leaching conditions were obtained by agitating at frequent intervals for the first hour, standing for an hour, and finally agitating again for the third hour.

2. Carrollite under the same conditions dissolved to the extent of less than 1 per cent.

3. While the oxide cobalt ores of the Belgian Congo were much more soluble in dilute acid saturated with SO_2 than Nkana ore, the addition of HF to the former was also necessary to recover all the cobalt.

EFFECT OF VARIABLES ON LEACHING PROCEDURE

A number of experiments were carried out on the effect of such variables as time, acid concentration, and agitation on the leaching procedure. Various oxide cobalt ores and carrollite were employed. Prolonging the leaching time beyond 3 hr. had little effect on the recovery of oxide cobalt or on the solubility of carrollite. Increasing the concentration of HCl from 10 to 30 per cent likewise had little influence on the extraction. A marked variation in the degree of agitation was brought about by placing a series of samples on the Ro-Tap machine and shaking continuously by this means for a

specified period. Again the differences in recovery were not significant.

EXPERIMENTAL RESULTS

A number of tests were run, leaching a mixture of the Nkana cobalt oxide ore and carrollite in varying proportions. The results of several, illustrated in Table 1, show that a mixture of the oxide and sulphide behaved in a manner similar to that found for the separate components.

TABLE 1.—*Leaching Tests with Mixture of Rhokana Cobalt Oxide and Sulphide Ores*

Treatment	Grams of Ore Taken		Grams Co Present in:		Grams Co Extracted
	Oxide	Carrollite	Oxide	Carrollite	
1 hr. agitation, 1 hr. standing, 1 hr. agitation 10 % HCl sat. with SO ₂ + few ml. HF..	2	0.10	0.0110	0.0234	0.0108
5 % H ₂ SO ₄ sat. with SO ₂ + few ml. HF..	2	0.15	0.0110	0.0350	0.0111

The procedure was tried on standard samples of mill feed and tailing at Rhokana Assay Laboratory. No special precautions were taken except that a large sample was necessary to insure reasonable accuracy. Representative results are given in Table 2.

The agreement between triplicates for this class of work is quite satisfactory, and indicates the degree of accuracy to be expected under routine analytical conditions. The agreement between the calculated oxide cobalt in the mixture of mill feed and oxide ore, and that recovered by leaching, is excellent.

Using the standard alpha-nitroso betanaphthol procedure for cobalt, a large sample is required for low quantities of oxide cobalt. By the use of a colorimetric procedure for cobalt employing nitroso-R-salt, the accuracy and ease of handling of

such determinations for small quantities of this element are greatly improved.

ACCURACY OF THE METHOD

While the leaching procedure developed for this method does not result in 100 per cent extraction of the oxidized cobalt and 0 per cent extraction of the sulphide cobalt, the figures 96 to 98 per cent for oxide and about 1 per cent for sulphide cobalt are considered very satisfactory. For nearly all Northern Rhodesian samples encountered in practice, the error from incomplete selectivity is negligible. Examples shown in Table 3 will illustrate the degree of accuracy of this procedure under varying ratios of oxide to sulphide cobalt.

When the oxide cobalt predominates, as it does in ores of the Belgian Congo, the percentage extraction of the oxide portion increases from a minimum of 96 to 97 per cent to nearly 100 per cent, thereby compensating in great measure for the error inherent in the procedure arising from incomplete extraction of the oxide cobalt. The accuracy, of course, is lessened at very low concentrations of oxide cobalt in the presence of very large quantities of sulphide cobalt, but even here the results, as shown by Table 3, are quite satisfactory for metallurgical purposes. It should be noted that while certain cobalt minerals can be leached almost completely by long contact with dilute acid in the presence of SO₂, the addition of hydrofluoric acid renders the procedure applicable to all types of oxidized cobalt ores.

RECOMMENDED PROCEDURE FOR THE DETERMINATION

As a result of our work on this subject at the Central Laboratory, and of co-operative work with Rhokana, Nchanga, and Union Minière laboratories, the following procedure is suggested for the determination of cobalt oxide.

Depending upon the quantity of oxide cobalt present in the material, and on the analytical method used for cobalt, select a weight of minus 200-mesh sample that

oxide or determined electrolytically, whereas if the colorimetric nitroso-R-salt procedure is employed on the same sample a weight of only 0.25 grams will suffice.

TABLE 2.—*Leaching Tests with Concentrator Products*

Sample	Total Co	Oxide Cobalt, Leaching Treatment			
		10 % HCl Saturated with SO ₂ + Few Ml. HF		5 % H ₂ SO ₄ Saturated with SO ₂ + Few Ml. HF	
		Wt., Grams	Per Cent, Av.	Wt., Grams	Per Cent, Av.
Mill feed, 25 grams.....	Per cent 0.14	0.0073 0.0072 0.0068	0.028	0.0068 0.0069 0.0068	0.027
	0.12	0.0033 0.0030 0.0031			
Mill tails, 25 grams.....	0.06	0.0063 0.0059 0.0070		0.0059 0.0062 0.0060	
Co oxide ore, 2 grams.....	0.55	0.0111 0.0110 0.0107	0.026	0.0110 0.0113 0.0112	0.024
Mixture of 25 grams feed + 2 grams oxide ore:..	Grams				
Calculated: from feed.....	0.0030				
From oxide ore.....	0.0110				
Total.....	0.0140				
Recovered.....	0.0145				
	0.0137				
	0.0141				
Average.....	0.0141		0.55		0.56

TABLE 3.—*Effect of Varying Oxide-sulphide Ratios on Accuracy of Procedure for Oxide Cobalt*

	Mill Feed 20 Grams, Oxide Cobalt, Per Cent			Geological Specimen 1 Gram, Oxide Cobalt, Per Cent		
	5	50	95	5	50	95
Percentage sulphide cobalt.....	0.133	0.07	0.007	5.70	3.00	0.30
Percentage oxide cobalt.....	0.007	0.07	0.133	0.30	3.00	5.70
Percentage total cobalt.....	0.14	0.14	0.14	6.00	6.00	6.00
Grams sulphide cobalt.....	0.0266	0.0140	0.0014	0.0570	0.0300	0.0030
Grams oxide cobalt.....	0.0014	0.0140	0.0266	0.0030	0.0300	0.0570
Grams total cobalt.....	0.0280	0.0280	0.0280	0.0600	0.0600	0.0600
Grams cobalt extracted:						
Sulphide cobalt.....	0.00026	0.00014	0.00001	0.00057	0.0003	0.00003
Oxide cobalt.....	0.00134	0.01344	0.02608	0.00285	0.0288	0.05586
Total cobalt.....	0.00160	0.01358	0.02609	0.00342	0.0291	0.05589
Percentage cobalt oxide found.....	0.008	0.068	0.13	0.34	2.91	5.59

will enable an accurate determination of cobalt to be made on the leached portion. For example, in a mill feed or tail running 0.02 per cent oxide cobalt at least 25 grams must be taken for the initial sample if cobalt is to be precipitated by alpha-nitroso beta-naphthol and weighed as

The ratio of leach solution to sample may vary quite widely, depending on the quantity of oxide cobalt present and on the other constituents of the ore. In general, add 25 ml. of 10 per cent HCl saturated with SO₂, or 5 per cent H₂SO₄ saturated with SO₂, to each gram of material in a

stoppered Erlenmeyer flask or covered beaker. When the initial effervescence and attack has subsided add 1 ml. HF per gram of sample.

Shake the flask or beaker for about $\frac{1}{2}$ min. every 10 min. for an hour, allow to stand an hour, and again agitate briefly at intervals of 10 min. for the third hour. Filter the sample through a Whatman No. 40 paper, using pulp, and wash thoroughly with hot water. Add 10 to 20 ml. 1:1 H_2SO_4 , if necessary, boil out SO_2 from the filtrate, and evaporate to fumes of SO_3 . Cool, dilute, boil to solution of salts, and precipitate copper and other group 2 elements with H_2S .

Filter off copper and other sulphides, and wash well with acidulated H_2S water. Boil out H_2S from the filtrate, and proceed with the determination of cobalt by any standard method. For gravimetric or electrolytic procedures iron may be separated by zinc oxide, ether, or sodium phosphate, and the cobalt precipitated with alpha-nitroso beta-naphthol and weighed as oxide, or deposited electrolytically. If the nitroso-R-salt method is employed, the filtrate, after oxidation of the iron with HNO_3 , is taken to fumes of SO_3 before proceeding with the development of the color in the usual manner.

SUMMARY

A procedure is described for the determination of oxidized cobalt in the presence of cobalt sulphide in ores and concentrator products. This differentiation is important in concentrating and other metallurgical operations of cobalt producers.

The method is based on the selective solvent action of dilute H_2SO_4 or HCl , in the presence of hydrofluoric acid and the reducing agent sulphurous acid, on oxide cobalt minerals.

The procedure gives a recovery of over 96 per cent of the oxidized cobalt with a contamination of less than 1 per cent of the cobalt sulphide present. Its accuracy for nearly all ratios of oxide: sulphide is therefore comparable with that of most routine chemical analyses.

It is believed that the method may be adapted for the differentiation of oxidized and sulphide forms of other elements in the mining and metallurgical industry.

ACKNOWLEDGMENT

The authors wish to express their appreciation of the cooperation extended by the management and laboratory staff of Union Minière du Haut Katanga in this investigation.

Laboratory Preparation of Lithium Metal by Vacuum Metallurgy*

By W. J. KROLL† AND A. W. SCHLECHTEN,‡ MEMBER AIME

(New York Meeting, March 1947)

As this paper is written, the only method for the commercial production of lithium metal is by the fusion electrolysis of LiCl-KCl mixtures, as first proposed by Guntz.² The details of the industrial process have not been made public but Osborg⁸ stated that an efficiency of more than 90 pct is obtained with a lithium metal recovery above 95 pct and that the metal is 99.5 pct pure. Pletenev⁹ gave a power consumption of 66 kw-hr per kilogram of lithium metal produced with a salt consumption of 9 kg of LiCl and 0.4 kg of KCl. Pletenev's figures indicate a somewhat lower recovery than that given by Osborg. In a recent report on German lithium plants, Motock⁷ gives figures that are also less favorable than those reported by Osborg. At the German plants the lithium recovery in electrolysis was only 83.4 pct, with a power consumption of 140 kw-hr per kilogram of lithium. The metal averaged only 97 pct pure, with sodium and potassium as the chief impurities. The presence of SO₂, SO₃, SiO₂, Ba, Ca, and appreciable amounts of Na and Fe₂O₃ were especially disturbing in the electrolysis, and it was necessary to run the cell for some time to eliminate most of these impurities and condition the bath.

It may be noted here that most of these impurities do not interfere with a thermal reduction process.

These facts show that the present method of producing lithium is fairly efficient and would suggest that other methods could not compete. However, fusion electrolysis has certain drawbacks, such as the necessity of supplying costly, low-voltage direct current and of collecting and processing the anodic chlorine if it is not to be wasted. An even greater disadvantage is that lithium chloride must be used for an electrolyte. It is one of the most expensive salts of lithium, since it cannot be produced in anhydrous form by precipitation from aqueous solution, as is done with LiF or Li₂CO₃.

The reduction of lithium by a vacuum process similar to the ferrosilicon method for the production of magnesium would have certain advantages. Small units such as Pidgeon retorts, would give flexibility of production to meet demand, and a small plant would require moderate capital outlay. There is a possibility of using idle Government-owned magnesium plants for such purposes. The raw materials needed for vacuum thermal reduction would not have to be extremely pure, especially with respect to the iron and calcium content.

This paper describes a series of experiments to determine the effectiveness of various agents for the reduction of lithium compounds. The investigation is part of a program of vacuum metallurgy con-

* Published by permission of the Director, Bureau of Mines, U. S. Department of the Interior. Manuscript received at the office of the Institute Dec. 19, 1946. Issued as TP 2179 in METALS TECHNOLOGY, June 1947.

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* References are at the end of the paper.

ducted at the Northwest Electrodevelopment Laboratory of the Bureau of Mines, U. S. Department of the Interior, at Albany, Oregon, under the supervision of B. A. Rogers, former chief of the Albany Division, Metallurgical Branch.

PREVIOUS WORK

Various proposals have been made for thermal reduction of lithium compounds. In Gmelin¹ it is stated that Warren reduced LiOH with magnesium, that Hackspill used calcium to reduce LiCl, and that Troost suggested sodium as a reducing agent for LiCl.

There are serious objections to all of these combinations. The reduction of LiOH with magnesium is violent, and the product is poor because hydrogen evolved by the reaction recombines with the lithium in the condenser. The volatility of magnesium is so nearly that of lithium that clean separation of the two metals appears to be impossible. The use of calcium as a reducing agent is hardly commercially feasible because of the high cost and high atomic weight of this metal. The reaction of lithium chloride and sodium rapidly reaches an equilibrium, with the production of very little lithium; high concentration of LiCl must be maintained, and the depleted salts must be reclaimed.

The reduction of LiCN with aluminum, iron, or magnesium has been proposed but does not seem promising because of the formation of the very stable lithium carbide. For the same reason, the reduction of lithium chloride, fluoride, or sulphide with CaC_2 or the reduction of lithium carbonate with carbon is likely to be ineffective.

GENERAL CONSIDERATIONS

Aluminum or silicon usually is taken as the reducing agent for the reduction of the alkaline earth metals according to Guntz process. The theory of the mecha-

nism of reduction by these two metals has been stated in a previous paper.⁴ The reaction with aluminum will not yield Al_2O_3 , but a monoaluminate will be formed with whatever base is present. Likewise, silicon will end as an orthosilicate. Thus, to prevent consumption of the metal oxide being reduced by combination with alumina or silica, it is necessary to add some other base, such as CaO. The addition of the lime also has the effect of keeping the reaction mixture loose and facilitates the escape of the metal vapors.

Other reducing agents could be used but have objectionable features for various reasons. Beryllium, cerium, and most metals of the fourth, fifth, and sixth group would be costly. Iron-group metals are effective as reducing agents only at very high temperatures. Other commercial compounds, such as calcium silicide, zirconium silicide, or ferroalloys of aluminum, chromium, vanadium, and titanium, have no price advantage over aluminum, silicon, or ferrosilicon.

The choice of reducing agent is governed by the compound to be reduced; for example, the relative halide affinities of the alkaline earth metals compared with that of aluminum are not in the same order as the oxide or sulphide affinities. For this reason, aluminum cannot be used for the reduction of lithium chloride, although it effectively reduces the oxide. One other point to be considered is the relative volatility of the reducing agent and the compound to be reduced. In a vacuum-distillation process, magnesium cannot be used to reduce lithium fluoride to lithium metal, because the magnesium will distill over with the reduced lithium metal at the temperature required for reduction, and an alloy will be obtained.

With these theoretical considerations in mind, it was decided that the greatest chance of success would lie in the vacuum

reduction of $\text{Li}_2\text{O}-\text{CaO}$ mixtures with Al and Si; of $\text{LiCl}-\text{CaO}$ mixtures with Si; and of $\text{LiF}-\text{CaO}$ mixtures with Si and Al. The production of Li-Mg alloys by reduc-

with an inner diameter of $2\frac{1}{8}$ in. (Fig 1). The tube was supported vertically with the closed end on top; a metal head was fastened by a wax seal to the lower end

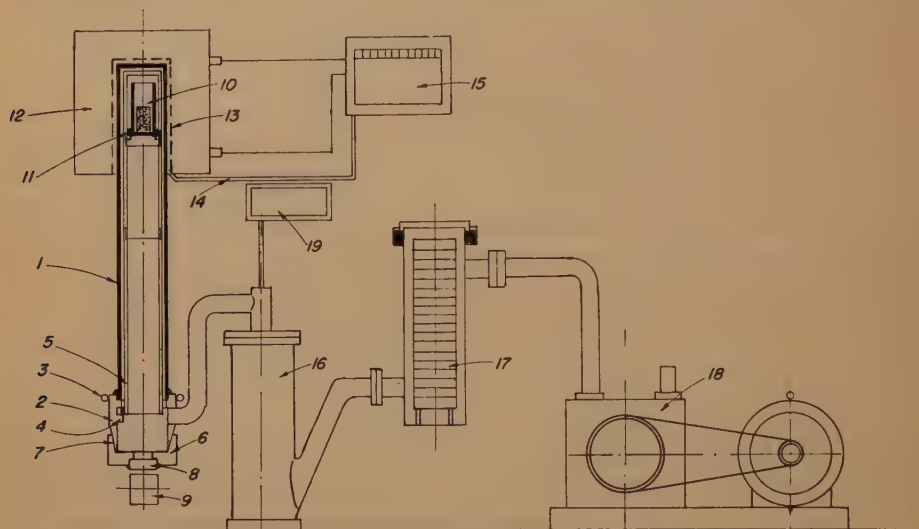


FIG 1—APPARATUS FOR THERMAL REDUCTION OF LITHIUM.

- | | |
|--------------------------|--|
| 1. Porcelain tube. | 11. Bayonet. |
| 2. Conical head. | 12. Metallic resistor furnace. |
| 3. Water cooling. | 13. Smith No. 10 alloy coil. |
| 4. Bayonet. | 14. Thermocouple leads. |
| 5. Insert. | 15. Temperature controller. |
| 6. Conical cover. | 16. Oil-diffusion pump. |
| 7. Ground joint. | 17. P_2O_5 drying tower. |
| 8. Glass window. | 18. Mechanical pump. |
| 9. Mirror. | 19. McLeod tilting gauge. |
| 10. Crucible with batch. | |

tion of $\text{Li}_2\text{O}-\text{CaO}$ mixtures with magnesium was also considered.

The heats of formation of certain compounds that would be involved are given in Table 1. These data are not encouraging for most of the proposed reductions, nevertheless it was felt that the volatility of lithium metal was so great that it would be possible to promote such endothermic reactions.

EXPERIMENTAL EQUIPMENT AND PROCEDURE

The vacuum furnace used for the experiments described in this paper consisted of a porcelain tube 40 in. long

of the tube. Vacuum connections were made through the metal head, which also had a vacuum-tight cover with a conical ground joint that could be opened for the introduction of samples into the tube. A mechanical pump in series with an oil-diffusion pump gave a vacuum of less than one micron in the system. The vacuum was measured with a Stokes tilting McLeod gauge.

Only the top 12-in. section of the tube was heated. The heating element was made of Smith No. 10 alloy wire wound on an Alundum core embedded in Alundum cement and insulated with diatomite brick. The temperature was measured

TABLE 1—*Heat of Formation, in Kilogram-calories*

$2\text{LiF} = 289.4$	$\text{MgF}_2 = 264.2$	$\frac{2}{3}\text{AlF}_3 = 166.0$	$\frac{1}{2}\text{SiF}_4 = 119.9$
$2\text{LiCl} = 197.4$	$\text{MgCl}_2 = 151.0$	$\frac{2}{3}\text{AlCl}_3 = 111.2$	$\frac{1}{2}\text{SiCl}_4 = 75.1$
$\text{Li}_2\text{O} = 143.0$	$\text{MgO} = 145.8$	$\frac{1}{3}\text{Al}_2\text{O}_3 = 119.3$	$\frac{1}{2}\text{SiO}_2 = 97.4$

at the outside wall of the porcelain tube and controlled by means of a platinum-platinum-rhodium thermocouple attached to a recording pyrometer controller. The use of the Smith No. 10 resistance wire made it possible to run at temperatures as high as 1300°C .

A sample to be heated was placed in a crucible, pushed up into the heated portion of the tube, and supported there on a small porcelain tube. If it was expected that there would be volatilization of some constituent or reaction product that would condense in the lower part of the furnace, the sample was placed in a crucible, which fitted inside a stainless-steel tube, which, in turn, slipped inside the furnace tube. With this arrangement, all condensate was caught inside the stainless-steel tube and was readily removed from the furnace.

The mixtures to be heated were first briquetted and then placed in a crucible in the furnace. The vacuum pumps were started and when a vacuum in the neighborhood of one micron was obtained the heating coils were turned on. The temperature was brought up slowly to the maximum desired and held there overnight. The operator could see the interior of the furnace through a small window in the metal head and observe whether or not a condensate was formed. After the run was completed, the furnace

was allowed to cool, and was opened. Any condensate was scraped from the tube; the tube was washed, and the washing solution was analyzed for lithium. The residue of the charge was removed from the crucible and weighed.

PRODUCTION OF LITHIUM OXIDE

Lithium oxide is not commercially available, but it can be produced by thermal decomposition of the carbonate or the hydroxide. Johnston³ gives dissociation pressures for the two compounds (Table 2).

The melting point of Li_2CO_3 is 732°C and that of LiOH is 455°C . They reach a dissociation pressure of 760 mm Hg at 1270°C and 924°C , respectively. Available data indicate that Li_2CO_3 is dissociated more easily than BaCO_3 but less readily than CaCO_3 .

Few data are available on the physical and chemical properties of Li_2O . It is said to be slightly volatile at 1000°C and to melt above 1625°C .

To obtain lithium oxide for reduction experiments, it was decided to produce it by thermal dissociation of Li_2CO_3 in a vacuum. The use of a vacuum furnace makes it possible to eliminate most of the CO_2 at a temperature slightly lower than the melting point of Li_2CO_3 . It would be possible to dissociate the Li_2CO_3 under an inert gas or with the addition of

TABLE 2—*Dissociation Pressures for Li_2CO_3 and LiOH ^a*

Temperature, deg C... Pressure, mm Hg.....	Li_2CO_3					LiOH				
	610 1	723 4	810 15	888 32	965 63	520 2	610 23	670 62	724 121	812 322

^a From Johnston.³

carbon or carbide, as is done with BaCO_3 , but the temperature required would be much higher than that of the vacuum method.

Consideration was given to the possibility of using LiOH rather than Li_2CO_3 , but the hydroxide is more expensive and melts at a lower temperature. Furthermore, the resultant moisture from the breakdown of the hydroxide would cause difficulty in the vacuum pumps.

As was mentioned before, if silicon or aluminum is to be used as a reducing agent for Li_2O , a strong base is required to combine with the SiO_2 or Al_2O_3 . With this in mind, CaO was added to the Li_2CO_3 before calcination.

Li_2CO_3 was mixed with $1\frac{1}{2}$ times as much CaO by weight; the mixture was briquetted and heated in the vacuum furnace. The first appreciable gas evolution was at 600°C . The temperature was maintained at 850°C until no more CO_2 was given off. After the furnace had cooled, the calcined material was removed and crushed to a powder. This product showed only a slight indication of melting.

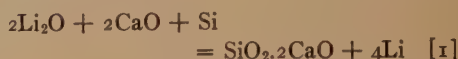
In a subsequent test, Li_2CO_3 was calcined without the addition of CaO . The gas evolution started at 600°C and the charge had to be heated to 820°C to drive off the CO_2 . At this temperature, which is above the melting point of the Li_2CO_3 , the contents of the crucible fused and a small amount boiled over. The product obtained contained only 0.31 pct carbon dioxide. The addition of CaO facilitates the evolution of CO_2 , the lime acting as a bulk material that keeps the passages open for the escape of the gases. The experiment shows that Li_2O can be obtained by thermal dissociation in vacuo more easily than BaO from its carbonate.

REDUCTION OF LITHIUM OXIDE

Reduction with Silicon

The reduction of mixtures of lithium oxide and calcium oxide with silicon,

by analogy with the similar reduction of dolomite with ferrosilicon, probably proceeds according to the following equation:



The ground mixture of Li_2O - CaO from the calcination described in the previous section was thoroughly mixed with finely pulverized silicon (100-mesh). A 10 pct excess of silicon was added over that indicated by Eq 1. The mixture was briquetted and heated in the vacuum furnace under a residual pressure of one micron or less. The furnace was held for 15 hr at the maximum temperature. The deposition of lithium metal in a ring in the cooler part of the furnace immediately below the heated zone could be observed through the small window at the lower end of the tube.

The results obtained are given in Table 3. The recoveries increased with increased temperature. At 850°C the efficiency was only 52.5 pct while at 1300°C it had reached 92.7 pct. For comparison, some of the data obtained with aluminum and magnesium as reducing agents have been included in the table.

These data would indicate that a reasonable recovery of lithium is obtained in the temperature range 950° to 1000°C and that an increase above those temperatures only slightly improves the recovery. The residual gas pressure obtained in commercial magnesium units is generally of the order of 50 microns. The lithium recoveries probably would be slightly lower in commercial units than those obtained in the laboratory furnace with a residual gas pressure of one micron.

An average sample of lithium metal made by the silicon reduction of a mixture of lithium oxide and calcium oxide in four different runs contained: 0.01 Si, 0.01 pct Al, and 0.04 pct Ca. The metal

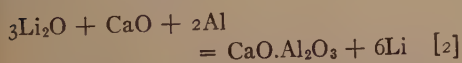
TABLE 3—*Reduction of Li₂O-CaO Mixtures*

TABLE 3 Reduction of Li_2O with Various Metals							
No.	Grams Lithium			Percentage of Lithium			Temperature, Deg C
	Input	Output	Residue	Recovery	Residue	Not Accounted for	
Silicon as Reducing Agent							
1	6.1	5.66	0.85	92.7	13.9	+6.6	1300
2	3.2	2.7	0.55	84.2	17.2	+1.4	1100
3	3.7	3.0	0.46	81.0	12.4	-6.6	960
4	8.2	6.0	1.97	73.2	24.1	-2.7	950
5	4.0	2.1	1.45	52.5	36.4	-11.1	850
Aluminum as Reducing Agent							
6	3.84	3.1	0.44	80.6	11.5	-7.9	900
Magnesium as Reducing Agent							
7	6.7	4.83	0.6	72.2	8.9	-18.9	950

produced in this way is of outstanding purity and presumably was also free of chlorine.

Reduction with Aluminum

The reduction of lithium oxide with aluminum resembles very closely the reduction with silicon. The following equation represents the probable reaction:



The experimental procedure was the same as that used with silicon; a 10 pct excess of aluminum above the theoretical amount required was added to the Li₂O-CaO mixture.

At a temperature of 900°C and under a vacuum of one micron or less, 80 pct of the lithium in the charge was recovered as metallic lithium.

It appears that approximately the same recovery is obtained with aluminum for the reducing agent as with silicon, but slightly lower temperatures can be used.

Reduction with Magnesium

The reduction of Li₂O with magnesium does not seem promising, since the vapor

pressure of magnesium is lower than that of lithium. The boiling point of lithium as given by Maucherat⁶ is about 1257°C, as compared with 1100°C for magnesium. Despite this apparent difficulty it was thought worth while to attempt the reduction, as the production of metallic lithium would depend upon the relative stability of MgO and Li₂O at the temperature of the experiment.

A mixture of 15.8 grams Mg, 19.8 grams Li₂O and 55.2 grams CaO was briquetted as in the previous experiments. In this instance, the CaO had no chemical function. The briquette was heated 2½ hr at 1000°C under a helium atmosphere, to allow the Li₂O and the magnesium to react. The furnace was then cooled and reheated slowly to 950°C with a vacuum of one micron. This temperature was maintained overnight and a metal mixture was found to have distilled over, which contained 51.6 pct Li; the remainder was magnesium. Of the lithium in the charge, 72.2 pct was recovered in the condensed alloy.

This experiment indicates that while it is possible to reduce Li₂O with magnesium, sufficient magnesium is distilled over to contaminate the product badly.

However, magnesium-lithium alloys can be made in this manner.

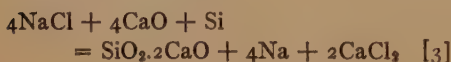
REDUCTION OF LITHIUM CARBONATE

The conversion of Li_2CO_3 to Li_2O and the subsequent reduction of the oxide in a separate run has been described. Two experiments were made to determine whether the calcination and the reduction could be accomplished in one operation.

The Li_2CO_3 , CaO , and the silicon were mixed in the same proportions as before, briquetted, and heated under vacuum at 750°C until all evolution of CO_2 ceased. The temperature was then raised to 950°C to promote the reduction reaction. A small amount of badly burned condensate was obtained, indicating that probably the lithium condensate had been oxidized by the CO_2 released from the Li_2CO_3 . Most of the silicon reacted with CO_2 before reducing the free Li_2O .

REDUCTION OF LITHIUM CHLORIDE

A process has been developed by one of the authors⁵ for producing metallic sodium from NaCl according to the following equation:



In this operation sodium is evaporated because it is more volatile than its chloride; the boiling points are, respectively, 850° and 1685°C . The margin of operation with lithium is not nearly as great; the metal boils at 1257°C and LiCl at 1384°C . Silicon can be replaced by aluminum.

Two runs were made with LiCl plus CaO mixtures to which silicon had been added as a reducing agent. In the first experiment the briquettes were heated to 850°C under a vacuum, and in the second experiment the briquettes were heated to 1000°C under helium and then cooled and reheated to 850°C under a vacuum. In both instances a large con-

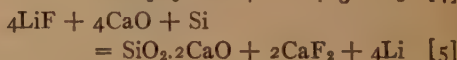
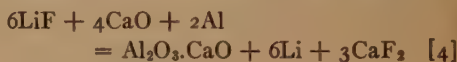
densate of LiCl was obtained, which contained no metallic lithium.

These experiments would indicate that LiCl is too volatile as compared with lithium to permit a successful reduction of the metal.

REDUCTION OF LITHIUM FLUORIDE

The reduction of lithium fluoride by the same reaction as that proposed for lithium chloride has more chance for success because the vapor pressure of LiF is low. Van Laar¹⁰ found that at 1390°C the vapor pressure was only 81 mm .

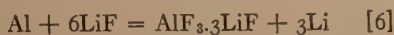
A run was made with LiF plus aluminum as the reducing agent; CaO was added, with the intention of tying up the fluorine of the lithium fluoride to make the formation of either AlF_3 or SiF_4 impossible. The probable reactions involved are:



At 1000°C a condensate was obtained that contained approximately 90 pct of the lithium as metal and the other 10 pct as LiF . The lithium recovery was 44.2 pct of the input. A similar run with silicon as reducing agent gave at 1100°C a lithium recovery of 22.7 pct. There was no formation of SiF_4 . In both cases lithium metal was produced, but it was contaminated with lithium fluoride. In Gmelin¹ a statement is credited to Speketer to the effect that LiF cannot be reduced in a vacuum with aluminum; the data given herein disprove that contention.

The boiling point of LiF is 1666°C , according to Gmelin, while, according to the same source, the boiling point of AlF_3 is 1294°C and the salt sublimes without melting. These data would indicate that aluminum fluoride would be found in the condensate rather than LiF . However, analyses of the condensate showed only a trace of aluminum. The appearance

of LiF in the condensate instead of the more volatile AlF_3 could be explained by the formation of the very stable lithium cryolite, which is not decomposed by CaO and in which the vapor pressure of AlF_3 is certainly reduced greatly, while excess LiF can evaporate. The true nature of the reaction would then be:



It appears that while the reduction of LiF with aluminum or silicon is possible, the metal condensate contains some LiF.

CONCLUSIONS

Lithium metal was produced readily by the reduction of Li_2O -CaO mixtures with silicon or aluminum in a vacuum of less than one micron and at temperatures of 950° to 1000°C . Under these conditions, recoveries of better than 75 pct of the lithium content of the charge were obtained with silicon as a reducing agent and better than 80 pct with aluminum. The temperature required for the reduction with aluminum is lower than that needed with silicon. Lithium can be made by this process at a temperature that is substantially lower than that employed in the production of magnesium by the ferrosilicon process.

Lithium carbonate dissociates readily in a vacuum. The evolution of gas starts at 600°C and is complete at 850°C in a vacuum of one micron. Since the carbonate melts at 732°C , interference of the fusion with the degassing takes place, and it is advisable to add CaO to keep the mixture loose. Calcium oxide is needed in the reduction step to tie up the silica as an orthosilicate and the alumina as a monoaluminate.

Lithium carbonate-CaO mixtures could not be reduced efficiently with silicon, and the small amount of metal obtained was oxidized badly.

Lithium chloride could not be reduced with silicon in presence of CaO because the lithium chloride was too volatile. Lithium fluoride can be reduced in the presence of CaO with aluminum or silicon, but the product is contaminated with lithium fluoride. No SiF_4 was formed with silicon, and with aluminum, no AlF_3 was found in the condensate.

Magnesium-lithium alloys can be made by reducing Li_2O -CaO mixtures with magnesium at 950°C .

It appears that lithium is produced more easily by vacuum methods than is magnesium, barium, calcium, or strontium. The laboratory methods described for the production of lithium could be used with little modification for the commercial production of this metal.

The outstanding purity of the lithium metal made by thermal reduction of mixtures of lithium oxide and calcium oxide with silicon or aluminum may be emphasized. Only very minor amounts of silicon, aluminum or calcium could be found in the condensate.

ADDENDUM

After this work had been completed and the article had been written, the National Defense Research Committee released reports PB24472 and PB24481, describing experiments done by the National Research Corporation on methods of producing lithium by the reduction of lithium compounds with ferrosilicon. Although the two entirely independent investigations do not concur in every respect, they both indicate the feasibility of producing lithium metal by such reactions.

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Vacuum Process for Preparation of Lithium Metal from Spodumene

By R. A. STAUFFER*

(Chicago Meeting, October 1947)

THE chief ore of lithium is spodumene, a lithium-aluminum silicate containing up to 3 pct lithium. The preparation of lithium salts from spodumene is costly because of the low concentration of the metal and the difficulty of separating it from the other alkali metals present. Dr. Kroll's and Dr. Schlecten's recent paper¹ has reviewed various methods proposed for preparation of lithium. It will be seen from this paper that the methods proposed to date have required one or another of the lithium salts as a raw material. The high cost of these salts has been the chief item of expense in the lithium metal produced. This situation has made it interesting to investigate the possibility of producing the metal directly from spodumene.

When spodumene is calcined at 1000°C in the presence of lime, lithium oxide is replaced in the ore as is evidenced by the fact that it may be leached from the reaction mixture with water.² Free energy calculations suggested that lithium oxide might be reduced with aluminum or silicon and the lithium produced distilled from the reaction mixture by heating to about 1000°C in a vacuum. These facts taken together suggested that it might be possible to prepare lithium metal directly from spodumene by heating a mixture of the ore, lime, and a suitable reducing agent in vacuum and distilling off the lithium metal as formed.

Manuscript received at the office of the Institute June 12, 1947. Issued as TP 2268 in METALS TECHNOLOGY, September 1947.

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A portion of the work described in this paper was conducted under OSRD contract No. OEM sr 930.

¹References are at the end of the paper.

THE REPLACEMENT OF Li_2O IN SPODUMENE

A series of experiments were undertaken to determine the ratio of lime to spodumene necessary to free substantially all the lithium oxide present in the ore.

The spodumene used in these experiments was supplied by Foote Mineral Co. in the form of powder of about 200 mesh. Analysis of the spodumene was as follows:

	Pct
SiO_2	62.7
Al_2O_3	29.9
Li_2O	4.9
Na_2O	0.89
CaO	0.75
MgO	0.49
K_2O	0.44

Lime (cp -200 mesh) was added in various ratios to spodumene and thoroughly mixed in a ball mill. Two hundred gram samples of spodumene-lime mixtures were charged loosely in fireclay crucibles and held at 1000°C in a gas-fired furnace for 5 hrs. The product in each case was ground to pass 140 mesh and then placed in a thimble in a soxhlet extractor. Extraction with water was carried on for 6 hrs. After this period the extract was reduced in volume by evaporation in order to precipitate dissolved lime and was then filtered and titrated with $\frac{1}{4}$ normal hydrochloric acid. After correcting for residual calcium oxide in solution, the alkali present was calculated as lithium oxide.

The results of these experiments are shown in Table 1 and Fig 1. At lime-spodumene ratios less than 1.5, the products were invariably fused. At the ratio of 1.5 and above, the product was loosely sintered with little evidence of fusion. When the ratio of lime to spodumene was three, replacement of alkali oxides in the

ore was found to be substantially complete. Analysis of the resulting calcine showed that 22.8 pct of the total was unreacted lime, giving a ratio of reacted lime to spodu-

VACUUM THERMAL REDUCTION

The results obtained in the foregoing experiments suggested that the addition of a reducing agent to a 3 to 1 lime-spodu-

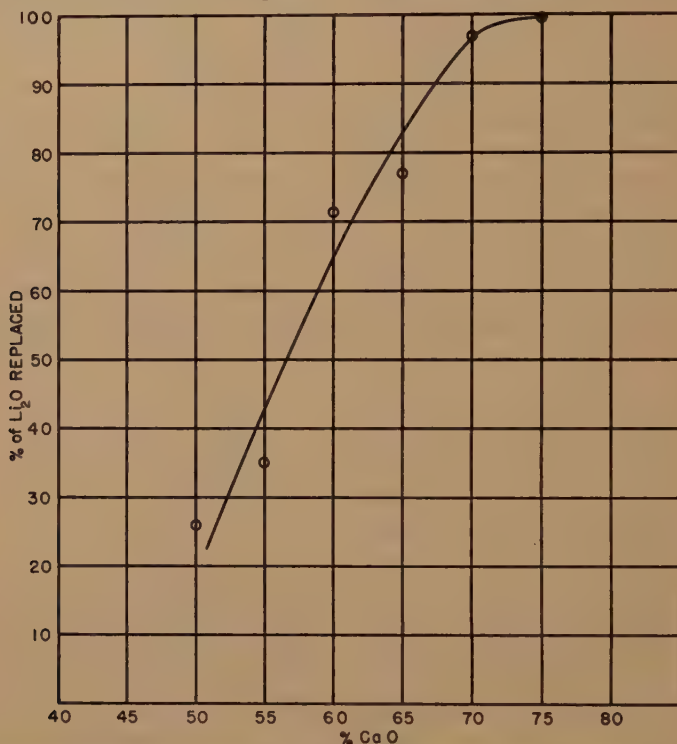


FIG 1—REPLACEMENT OF ALKALI OXIDE (Li_2O) IN SPODUMENE AT 1000°C , VS PCT CaO IN REACTION MIXTURE.

mene of 2.09 to 1. The reaction products aside from Li_2O are not known, but the above data indicate that between 7 and 8 moles of CaO react with each mole of spodumene ($\text{Li Al}(\text{SiO}_3)_2$).

mene mixture would produce lithium metal upon heating in vacuo.

EXPERIMENTAL APPARATUS AND PROCEDURE

TABLE 1—Replacement of Alkali Oxide in Spodumene by Calcine at 1000°C with Lime (alkali reported as Li_2O).

Pct CaO in Charge	Pct in Li_2O Freed	Condition Product
50	25.8	fused
55	34.9	fused
60	71.3	closely sintered
65	76.8	sintered
70	97.8	loosely sintered
75	99.5	loosely sintered

In order to investigate the preparation of lithium from lime-spodumene mixtures, the apparatus shown schematically in Fig 2 was constructed. This equipment consisted of a bottle-shaped stainless steel retort 20 in. long and 4-in. diam tapering down to 2-in. diam. A collar was provided in the retort against which a steel sleeve for collecting lithium was placed. A flange was provided for attachment of a sight glass and a side arm installed for attachment to a

pumping system. The pumping system consisted of a Central Scientific Megavac mechanical pump connected to the retort by 1-in. steel pipe. A National Research

microns, the furnace was turned on. The retort was brought up to desired operating temperature in $\frac{1}{2}$ hr and held for the desired cycle at this temperature. At the

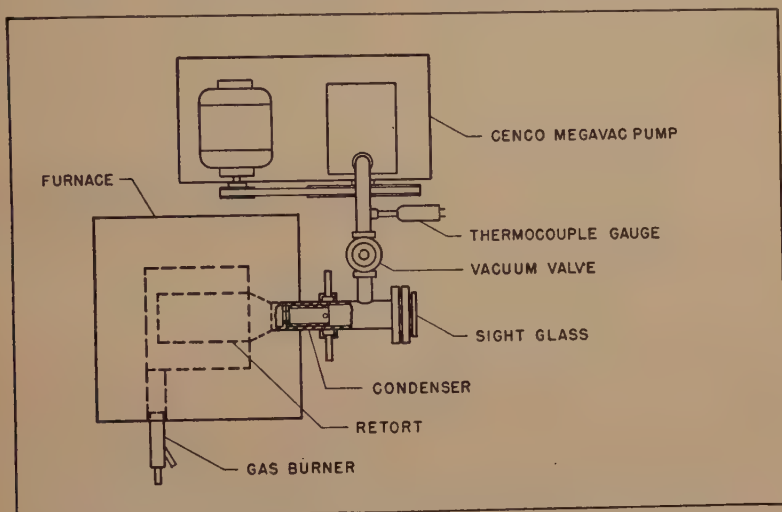


FIG 2—PLAN VIEW. LABORATORY EQUIPMENT FOR REDUCTION OF SPODUMENE.

Type-D thermocouple gauge and a Stokes tilt-type McLeod gauge were provided for pressure determination.

The retort was heated by means of a small gas-fired furnace built from insulating firebrick and equipped with laboratory blast burners. Temperature was measured by a chromel-alumel thermocouple and a Brown indicator, this being checked periodically by an optical pyrometer. The apparatus was capable of reaching 1200°C with pressure in the retort ranging from 0.010 to 0.025 mm of Hg.

The procedure in conducting a run was as follows: Approximately 1 kg of the mixture to be treated was briquetted in a Type-R Stokes briquetting press and charged into the bottle-shaped retort. The collection sleeve was dropped in against the supporting shoulder, the sight glass flanged bolted in place, the retort slipped into the furnace and attached to the pumping system. Pumping was started, and water was run into the cooling jacket of the retort. When the pressure reached 10 to 25

microns, the furnace was turned off and allowed to cool. When the collecting sleeve was approximately at room temperature, the apparatus was dismantled. The collecting sleeve was weighed, the lithium dissolved out of the sleeve by treatment with a mixture of ethyl alcohol and water, and the empty sleeve dried and reweighed. The solution of lithium hydroxide was titrated with standard oxalic acid solution to determine alkali metal content, this being assumed lithium metal.

The spodumene used in these experiments was received in the form of 200 mesh powder from Foote Mineral Co. Two hundred mesh cp lime was used. Ferrosilicon, 200 mesh, analyzing approximately 75 pct silicon, was purchased from Electrometallurgical Corp. Cp Aluminum was added in the form of 100 mesh powder.

Experiments were conducted to determine the conditions necessary to obtain a high yield of lithium metal from spo-

mene. Ferrosilicon and aluminum were compared as reducing agents. The characteristics of the product were investigated.

RESULTS

When lime, spodumene, and a reducing agent are heated in a vacuum, there is at

tassium are also volatilized from the reaction mixture, but the vapor pressure of these elements is higher than lithium,³ and they pass through the collecting sleeve, condensing in a cooler region. (Fig 3.)

Reaction temperature for aluminum and ferrosilicon reduction are essentially the

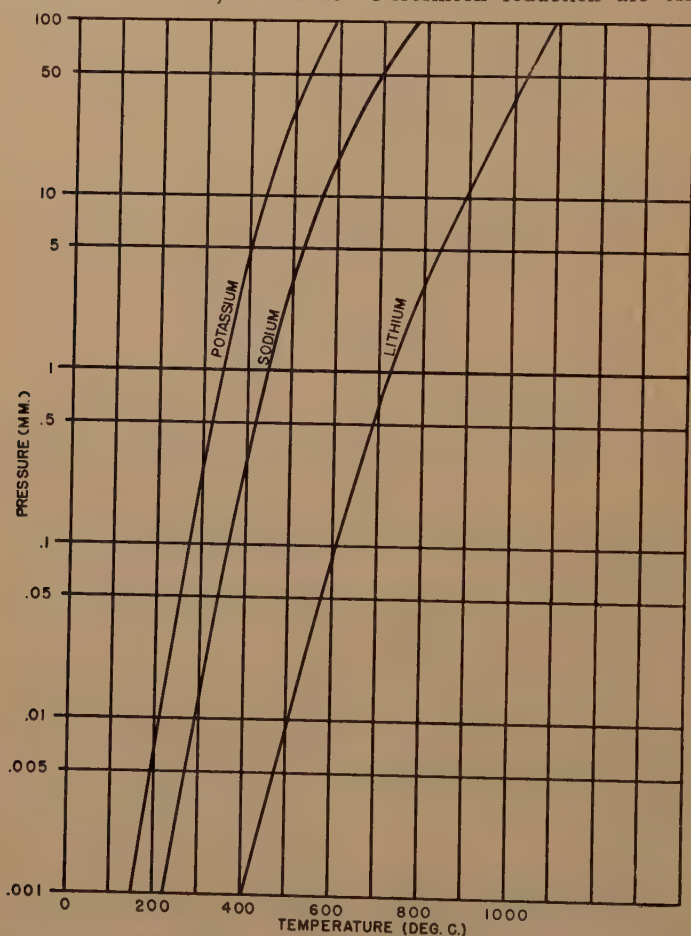


FIG 3—VAPOR PRESSURE (MM OF HG) VS TEMPERATURE (°C) FOR ALKALI METALS.

first a pressure rise while the charge is degassed, then the pressure falls off, and at around 1000°C and 25 microns pressure lithium metal begins to distill out of the reaction mixture. The metal may be condensed by holding the collecting sleeve at approximately 450°C. Sodium and po-

same. Lithium begins to distill at about 1000°C, but for high yields it is necessary to run at between 1050 and 1150°C. There is a significant difference in lime requirement between aluminum reduction and ferrosilicon reduction. In order to recover more than 85 pct of the lithium in spo-

mene, it is necessary to use a lime-spodumene ratio of 2.3 for ferrosilicon reduction while only 1.5 is required for aluminum. (Tables 2 and 3.)

TABLE 2—*Direct Reduction of Spodumene by Ferrosilicon in 2-in. Diameter Retort*

Pct yield lithium vs ratio $\frac{\text{CaO}}{\text{Spodumene}}$ in charge

$$\frac{\text{FeSi}_2}{\text{Spodumene}} = 0.135$$

Reaction Temperature 1050 to 1150°C
Collection Time = 2 hours

$\frac{\text{CaO}}{\text{Spodumene}}$	Pct Yield of Lithium	Average Pct
1.4	34.4 42.5	38
1.5	43.6 49.8 39.8	47
	53.9 49.6	
1.8	47.5 55.4	51
2.00	47.1 71.4 58.0	71
	86.4	
2.2	69.2 73.2	70
2.3	66.6 91.7 84.0	87
	86.1 84.5	

TABLE 3—*Direct Reduction of Spodumene by Aluminum in 2-in. Diameter Retort*

Pct yield lithium vs ratio $\frac{\text{CaO}}{\text{Spodumene}}$ in charge

$$\frac{\text{Al}}{\text{Spodumene}} = 0.2$$

Reaction temperature 1050 to 1150°C.
Collection Time = 2 hours

$\frac{\text{CaO}}{\text{Spodumene}}$	PCT YIELD OF LITHIUM
1.0	53.0
1.3	67.2
1.5	92.2

The theoretical weight ratio of reducing agent to spodumene required for reduction of alkali metals in the ore was calculated to be 0.037 in the case of ferrosilicon and 0.035 in the case of aluminum. In practice a large excess over these values was found necessary. As shown in Tables 4 and 5 the required ratio for ferrosilicon is about 0.14 and that for aluminum 0.2. The need for

this excess has been traced to the water content of the lime used in replacement. It has been found that the concentration of reducing agent in the charge is seriously depleted by reaction with water held in the lime. The variation of water content of lime from one run to another accounts in part for the wide variation of yield results in Tables 2, 4, and 5.

TABLE 4—*Direct Reduction of Spodumene by Ferrosilicon in 2-in. Diameter Retort*

Pct yield lithium vs ratio $\frac{\text{FeSi}_2}{\text{Spodumene}}$ in charge

$$\frac{\text{CaO}}{\text{Spodumene}} = 2.34$$

Reaction temperature = 1050 to 1150°C
Collection time = 2 hours

$\frac{\text{FeSi}_2}{\text{Spodumene}}$	Pct Yield of Lithium	Average Pct
.04	48.7 35.1 33.2	41
	46.8	
.10	47.8 40.9 48.1	44
	38.5	
	58.2	
.14	32.8 91.7 84.0	87
	86.1 84.5	

TABLE 5—*Direct Reduction of Spodumene by Aluminum in 2-in. Diameter Retort*

Pct yield lithium vs ratio $\frac{\text{Al}}{\text{Spodumene}}$ in charge

$$\frac{\text{CaO}}{\text{Spodumene}} = 1.5$$

Reaction temperature = 1050 to 1150°C
Collection time = 2 hours

$\frac{\text{Al}}{\text{Spodumene}}$	Pct Yield of Lithium	Average Pct
0.01	13.6 14.5	14
0.10	64.0 69.7	67
0.2	92.2	92.2

The effect of pressure in the reaction vessel was demonstrated in several cases when pump failure occurred during runs.

It was found that at pressures in excess of 100 microns, yields are low and the product is badly contaminated with nitride and oxide.

Apparatus and Procedure

The apparatus used in this investigation is shown schematically in Fig 4. It is very similar to that used for experimental work

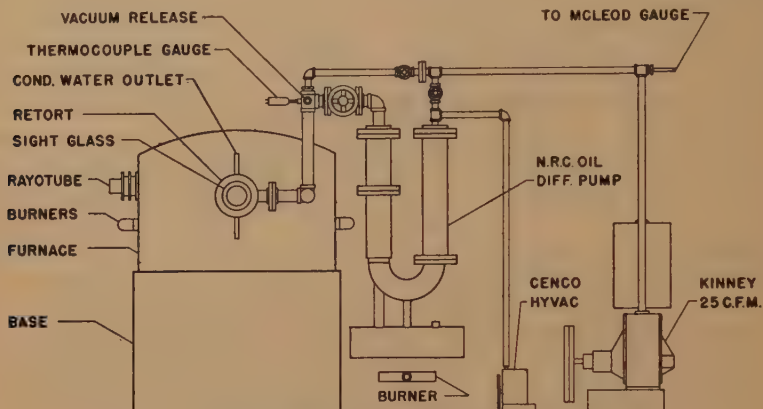


FIG 4—FRONT ELEVATION OF SIX-INCH RETORT FURNACE.

Lithium can be prepared from a loose, unbriquetted charge, though much difficulty is encountered in the blowing of the charge during evacuation, and the yields obtained by this technique are low. Similarly, addition of a solid, unpulverized reducing agent separate from the lime-spodumene mixture does produce lithium but gives low yields.

The lithium produced collects in a pool on the bottom of the condenser. When removed from the furnace, it has a bright metallic luster, but after short exposure to air, it is darkened by reaction with oxygen and nitrogen. Analysis of the product ranges from 85 to 90 pct lithium. The major impurity is magnesium. Some aluminum is present when this metal is used as a reducing agent.

INVESTIGATION OF THE PREPARATION OF LITHIUM FROM SPODUMENE ON A LARGER SCALE

Since experimental results in the preparation of lithium directly from spodumene appeared promising, equipment was assembled to test the process on a somewhat larger scale.

but considerably larger. The retort consisted of a 35-15 nickel-chrome steel casting 40-in. long, 6-in. id and 7-in. od welded to a mild steel condensing assembly. The retort was evacuated by a specially designed National Research Corp. 6-in. diffusion pump backed by a 25 cfm Kinney mechanical pump. A Central Scientific Megavac was used to hold the diffusion pump, while the 25 cfm Kinney pump was used to rough the retort down from atmospheric pressure to the range where the diffusion pump became effective (about 1,000 microns). Using the diffusion pump, it was possible to maintain the retort at less than ten microns even when at maximum temperature. Pressure in the retort was read by means of a National Research Corp. thermocouple gauge used in conjunction with a Leeds and Northrup recording potentiometer, thus permitting a continuous record of pressure changes.

The retort was heated in a gas-fired furnace. Temperature was read and controlled by means of a Leeds and Northrup rayotube used in conjunction with a recorder-controller.

Experiments conducted in this furnace were concerned only with ferrosilicon reduction of spodumene. Charges ranged from 20 to 25 lb of briquettes. Spodumene used was obtained from Foote Mineral Co. as in the case of smaller runs. Ferrosilicon was obtained from Electrometallurgical Corp., the commercial 75 pct grade being used. A commercial grade of lime was used in place of the c.p. material used in experimental work.

In conducting a run, the system was sealed off, evacuated, and then brought up to desired operating temperature. At this point the system was vented, the charge of spodumene, ferrosilicon, and lime put into the retort with the aid of a long-handled scoop, the collector positioned, the system sealed off and evacuated. Reaction time was counted from the time when the retort had recovered from the heat loop produced by addition of the charge. At the end of the operation, the pumps were valved off from the retort, the retort vented, opened, and the collecting sleeve removed. The spent charge was removed by means of the long-handled metal scoop. The lithium produced was scraped from the collecting sleeve, weighed, and analyzed. The residue from the retort was ground, sampled, and analyzed for lithium, thus providing a second means of calculating yields. All runs in the 6-in. retort were conducted by charging and discharging without dropping retort temperature, differing in this respect from the smaller experimental operations.

RESULTS

The purpose of the 6-in. retort furnace was twofold. First, it was desired to show that the charge composition determined in experimental runs was applicable to large-scale operation; second, to investigate the effect of charge size, reaction temperature, and reaction time on yield.

Initial runs were made using the charge composition found suitable in experimental

runs, namely, 28.8 pct spodumene, 3.9 pct ferrosilicon, and 67.3 pct lime. In these experiments, charge weight was arbitrarily set at 20 lb. Reaction temperature was chosen as the maximum safely attainable without very frequent retort failure, that is, 1150°C. The charges were held at temperatures in excess of 1100°C for 3 hrs. Runs carried out under these conditions at first gave yields in the vicinity of 80 to 85 pct. However, yields dropped off over a period of a week, and these phenomena were finally traced to water pick-up in the lime used. It was shown that high yields could be obtained if lime was calcined before use in the reduction furnace.

On the basis of the foregoing experiments it was concluded that the charge composition determined in experimental runs was suitable provided freshly calcined lime was used. Rather than calcine all lime used in further experiments, it was decided to increase the concentration of ferrosilicon to compensate for the water contained in the lime. Accordingly, in studying the effect of charge size, reaction temperature, and reaction time on yield, the charge composition used was as follows: 27.7 pct spodumene, 7.8 pct ferrosilicon, 64.5 pct lime.

Yields in preliminary runs in the 6-in. retort were calculated both on the basis of weight and analysis of the product and on the basis of lithium content of the spent charge. Because of the crude collection unit used, namely, a removable metal sleeve in which the lithium collected in a puddle at the bottom, much difficulty was encountered in effecting complete removal of the metal. For this reason yield figures based on product weight and analysis ran 5 to 10 pct lower than those based on analysis of the spent charge. In several runs particular care was taken to effect complete removal of lithium from the collector, and it was shown that the yields in these cases agreed within 1 pct with those based on analysis of the spent charge. Yields calculated from lithium remaining in the spent charge are thus

considered more reliable than those based on product weight and analysis and have been used exclusively in the accompanying tabulations of results.

TABLE 6—*Direct Reduction of Spodumene by Ferrosilicon in 6-in. Diameter Retort*
Pct yield lithium vs reaction time

$\frac{\text{CaO}}{\text{Spodumene}} = 2.33$ $\frac{\text{FeSi}_2}{\text{Spodumene}} = 0.28$
Reaction temperature = 1150°C
Charge wt. 20 lb

Reaction Time	Pct Yield of Lithium	Average Pct
$2\frac{1}{2}$ hrs	91	
	91	91
2 hrs	91	91
	92	
1 hr	82	73
	64	

Yield vs reaction time was studied for a reaction temperature of 1150°C and charge weights of 20 lb. Results given in Table 6 and Fig 5 summarize this work and indicate that substantially all lithium may be reclaimed after 2 hrs of reaction time.

A second series of runs was conducted to investigate the effect of reaction temperature. Reaction time in these runs ranged from 2 to 3 hrs. The runs were divided into two groups. In one group of runs the furnace was charged to capacity, about 25 lb. In the other group 20 lb charges were used. Results are shown in Table 7 and Fig 6. Consistently higher yields were obtained with 20-lb charges indicating that space should be allowed above the charge to facilitate removal of lithium vapor. The

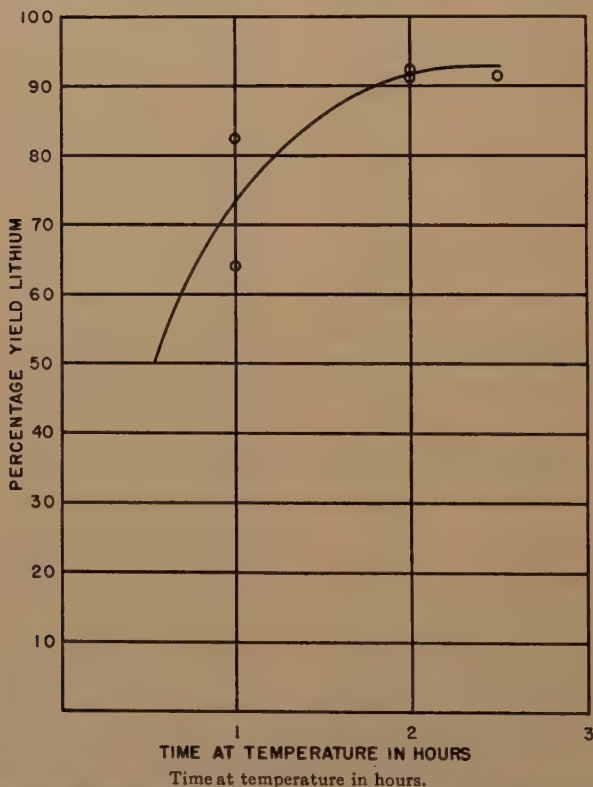


FIG 5—DIRECT REDUCTION OF SPODUMENE BY FERROSILICON YIELD VS REACTION TIME.

20 pound charges
27.7 pct Spodumene
7.8 pct Ferrosilicon
64.5 pct Lime. Temp. of runs approx. 1150°C .

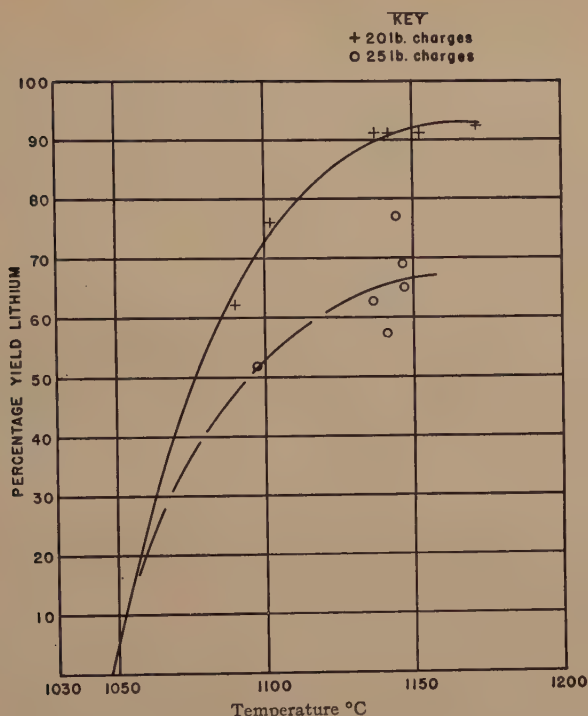


FIG 6—DIRECT REDUCTION OF SPODUMENE BY FERROSILICON YIELD VS REACTION TEMP. (°C).

Charge Composition
27.7 pct Spodumene
7.8 pct Ferrosilicon
64.5 pct Lime

results indicate that reaction temperature should be as high as possible, consistent with reasonable retort life.

TABLE 7—Direct Reduction of Spodumene by Ferrosilicon in 6-in. Diameter Retort

Per cent yield of lithium vs reaction temperature

$\frac{\text{CaO}}{\text{Spodumene}} = 2.3$ $\frac{\text{FeSi}_2}{\text{Spodumene}} = 0.28$
Reaction time = 2 to 3 hrs

Charge Wt.	Reaction Temperature Degrees Centigrade	Pct Yield of Lithium
20 lb	1047	0
	1047	0
	1090	62
	1102	76
	1137	91
	1142	91
	1152	92
	1171	52
25 lb	1097	47
	1141	73
	1144	55
	1140	69
	1147	69
	1147	69

DISCUSSION OF RESULTS

The experiments outlined have demonstrated that it is technically feasible to prepare lithium metal by reacting a mixture of spodumene, lime, and either ferrosilicon or aluminum in a vacuum furnace. The material produced is not comparable in purity to that produced by the electrolytic process, analyzing only 85 to 90 pct lithium metal. The work was carried on under Government contract which did not require that a high purity lithium be produced, and only meager attempts at purification have been made, though these have demonstrated that purity may be improved by vacuum distillation of the metal.

The apparatus used in experiments was patterned after that used in preparation of magnesium metal by the Pidgeon process. As mentioned previously, the collector used

was unsatisfactory for collection of molten metal though it had performed suitably when dealing with magnesium which collects in the solid phase. A more suitable collector was designed to permit drainage of the lithium into pigs, but work had to be terminated before this could be tested.

Although tests were conducted on a fairly small scale, the charge being only 25 lb and the product weight ranging from $\frac{1}{4}$ to $\frac{1}{3}$ lb, the agreement between operation in this furnace and in the 2-in. tubes used in preliminary experiments was sufficiently good to warrant extrapolation for purposes of preliminary cost estimates. With cost estimates based on the actual performance of magnesium plants using the Pidgeon process and allowing for redistillation of the lithium as a means of purification, it was shown that this process has promise of producing lithium metal more cheaply than the electrolytic process. Recent developments in design of vacuum furnaces may make this situation even more hopeful.

SUMMARY

1. Experiments were carried out to determine the conditions under which lithium oxide in spodumene may be replaced by lime. Results indicate that between seven and eight moles of lime react per mole of spodumene in replacing lithium. It was found that a substantial excess of lime is required for a high yield of lithium oxide and that the reaction will take place at temperatures as low as 1000°C.

2. Experiments were conducted to determine whether the addition of a reducing agent to a lime-spodumene mixture when heated in vacuum would produce lithium from the lithium oxide freed by the lime. It was found that such a reaction can be carried out with good yield of lithium, though the metal is of lower purity than that produced by the electrolytic process.

3. Experiments were conducted to determine whether the vacuum thermal re-

duction of spodumene has commercial possibilities. Although additional research is required to investigate purification of the metal and design of more efficient furnaces, there is reason to believe that the process may produce lithium metal more cheaply than the electrolytic method.

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2. J. W. Mellor: Comprehensive Treatise of Inorganic and Theoretical Chemistry, (1922-1937) 2, 443.
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DISCUSSION

(W. A. Dean and J. H. Scaff presiding)

D. J. MACK*—I am very glad to see this paper by Mr. Stauffer in addition to a paper on the same general subject by Kroll and Schlechten which was presented at the New York meeting in March. This is because it has clarified an idea which I had several years ago and which has bothered me ever since. You will recall that during the early days of the war there was a mad scramble to increase magnesium production and it was finally decided to use the Pidgeon process. In this process dolomite is reduced by ferro-silicon at high temperature under high vacuum. In the pilot plant studies using dolomite from various deposits it was found that some dolomites could not be used because the Na_2O and K_2O content was too high. These oxides were apparently also reduced by the silicon and the metallic sodium and potassium distilled over with the magnesium causing serious fires when the retorts were opened. This immediately suggested to me that it might be possible to produce commercially the alkali metals by a process similar to the Pidgeon process.

The paper presented by Mr. Stauffer has shown that such production is not only possible but is probably commercially feasible. Mr. Stauffer, was direct reduction of spodumene without lime attempted?

* University of Wisconsin.

R. A. STAUFFER (author's reply)—Direct reduction of spodumene without lime was attempted but failed. There was no evidence of reduction under these conditions, and at temperatures of the order of 1000 to 1100°C the entire charge fused.

D. J. MACK—Did you try other reducing agents such as silicon, calcium-silicon or metallic calcium?

R. A. STAUFFER—In addition to aluminum and ferro-silicon we did try metallic iron but found that it would not produce lithium metal.

D. J. MACK—Did you ever try to relate the yield of lithium to a calcium-silicon ratio rather than to just the amount of CaO used? In other words, the lime-silica ratio used in the preliminary treatment of the spodumene and then computing yield on the basis of the silicon in the ferro-silicon which presumably reacted with the Li_2O ?

R. A. STAUFFER—All we did in this respect was to look over equilibrium diagrams and to search out compounds which might help to explain the ratio of lime to spodumene used in the reaction.

D. J. MACK—Have you devised any theory of the mechanism of the reduction process?

R. A. STAUFFER—As far as we are able to ascertain, the reaction proceeds in several steps: Lime reacts with spodumene to replace

and free lithium oxide which is contained; the lithium oxide is reduced by means of aluminum or ferro-silicon; as alumina or silica are accumulated from this reaction they tend to combine to form lithium silicate or lithium aluminate, thereby tending to stop reduction. If sufficient lime is present it proceeds to break these compounds and tie up alumina and silica, freeing lithium oxide for further reduction. Beyond this we have not postulated a mechanism for the reaction.

J. H. SCAFF*—I have two questions I should like to ask Mr. Stauffer: (1) Would you care to give us an estimate of the cost of lithium produced by this process? (2) What are the impurities in the materials produced in the 6-in. retort?

R. A. STAUFFER—Operating a plant producing approximately 100 lb a day, it might be possible to produce for \$5 per lb. Impurities in the product as produced in the 6-in. retort include magnesium, aluminum, some silicon, and potassium. Of these the only troublesome one is magnesium. As far as the cost is concerned, the electrolytic process starts at some disadvantage as compared with spodumene reduction. The lithium in spodumene is worth about 60¢ per lb. The lithium in lithium chloride is worth between \$5 and \$6 per lb.

* Bell Telephone Laboratories, Murray Hill, N. J.

The Dithionate Process for Recovery of Manganese from Low-grade Ores

By S. F. RAVITZ,* MEMBER A.I.M.E., W. F. WYMAN,* A. E. BACK,* AND K. E. TAME*

(New York Meeting, March 1947)

IN 1940, when it appeared that the United States soon might be cut off from foreign sources of high-grade manganese ore, the Bureau of Mines began an extensive series of investigations on the production of ferro-grade products from low-grade domestic ores by ore-dressing, pyrometallurgical, and hydrometallurgical methods. Among the hydrometallurgical processes for oxide ores investigated was a sulphur dioxide process in which the manganese was recovered from solution by precipitation with lime;¹ this process is essentially as follows:

The ground ore is suspended in water and leached with SO_2 gas to extract the manganese as manganese sulphate. Calcium chloride is then added to the slurry to precipitate calcium sulphate and form manganous chloride solution, and the resultant slurry is filtered to remove the calcium sulphate together with the insoluble portion of the ore. Calcium hydroxide is added to the filtrate and the mixture is agitated with air to precipitate hydrated oxides of manganese and regenerate calcium chloride. The precipitate is calcined, and the calcium chloride is recycled.

To determine manganese extraction, reagent consumption, grade of product, and similar data for this process, a labora-

tory investigation was started. Two minor modifications in the process were soon made: (1) the ore was suspended in calcium chloride solution instead of in water in order to extract the manganese and precipitate the calcium sulphate in one step, and (2) the agitation with air after the addition of slaked lime to the filtrate was omitted because manganese hydroxide is readily precipitated without air agitation and can be nodulized or sintered to a satisfactory product. When the process was carried through a series of cyclic tests, it was noted that the concentration of dithionate ion (which is one of the products of oxidation of SO_2 by MnO_2) in the cycled solution gradually increased; at the same time the chloride content of the solution gradually decreased, owing to soluble losses in the leach residue and in the precipitate. After a number of cycles, the calcium chloride became virtually completely replaced by calcium dithionate, the quantity of dithionate ion formed during the leach being more than enough to make up for the losses of dithionate in filtering. The calcium chloride process thus developed into a calcium dithionate process. Since the latter eliminated the need for make-up calcium chloride, and the dithionate solutions appeared much less corrosive than the chloride solutions, work on the calcium chloride process was dropped in favor of the calcium dithionate process.

ACKNOWLEDGMENTS

The dithionate process was developed by the Bureau of Mines as part of a

Published by permission of the Director, Bureau of Mines, U. S. Department of the Interior. Manuscript received at the office of the Institute Dec. 29, 1945. Issued as TP 2064 in METALS TECHNOLOGY, September 1946.

* Metallurgist, Salt Lake City Division, Metallurgical Branch, Bureau of Mines, Salt Lake City, Utah.

¹ References are at the end of the paper.

broad program of metallurgical investigations on domestic manganese ores organized by R. S. Dean, Assistant Director, in 1940 and consolidated under his direc-

Acknowledgment is due also to the American Smelting and Refining Co. and to W. G. Rouillard, superintendent of the Garfield smelter, for permission

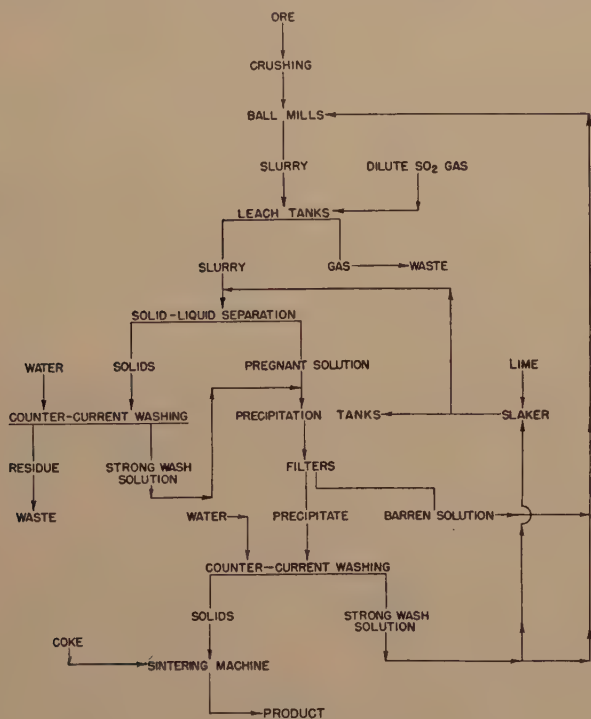


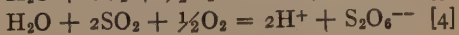
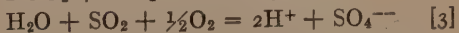
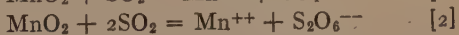
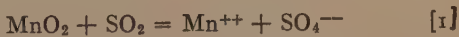
FIG. 1.—FLOWSHEET OF DITHIONATE PROCESS.

tion in 1942 with a similar program of mining investigations. The first work on the process was done by R. L. Evans, and the early laboratory work was supervised by F. S. Wartman. Among the others who took an active part in the experimental work were L. C. Bauerle, J. L. Dewey, A. L. Fox, J. D. Prater, Ruth Taylor, G. C. Ware, and D. F. Williams. S. R. Zimmerley, chief of the Salt Lake City Division, Metallurgical Branch, made many helpful suggestions and arranged for the mining and shipping of the various ore samples studied. Cyanidation and flotation tests on the leach residues were carried out by T. G. Chapman, consulting metallurgical engineer to the Bureau, and by H. G. Poole and W. G. Sandell.

to construct and operate a small experimental leaching plant at the smelter.

CHEMISTRY OF THE DITHIONATE PROCESS

A diagrammatic flowsheet of the process is shown in Fig. 1. A slurry of the ore in an excess of calcium dithionate solution is treated with gas (for instance, waste smelter gas) containing SO_2 and oxygen. Manganese sulphate, manganese dithionate, sulphuric acid, and dithionic acid are formed by the following overall reactions:



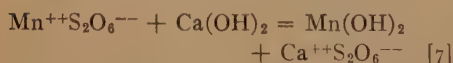
The sulphate formed by reactions 1 and 3 is immediately precipitated as calcium sulphate by reaction with the calcium dithionate present in the solution:



The intermediate oxides, Mn_2O_3 and Mn_3O_4 , which may be present in the ore, behave largely as though they were mixtures of MnO_2 and MnO , the latter being dissolved by the acid formed in reactions 3 and 4:



At the end of the leach, the solids, which consist of the insoluble portion of the ore and the precipitated calcium sulphate, are separated from the solution and discarded (or treated further if they contain appreciable quantities of lead, gold, or silver). The solution, which contains manganese dithionate, a small quantity of dithionic acid, and the excess of calcium dithionate, is treated with slaked lime to precipitate manganese hydroxide and regenerate the calcium dithionate:



The precipitate is filtered off and nodulized or sintered to produce manganese oxide, and the calcium dithionate solution is recycled. The only losses of dithionate are those due to incomplete washing of the leach residue and the manganese hydroxide precipitate. To maintain the dithionate concentration in the circuit, the quantity of dithionate formed by reactions 2 and 4 should be at least equal to such losses.

The dithionate ion is surprisingly stable, particularly when compared with sulphite ion and the various polythionates. Yost and Pomeroy² have shown that the rate of oxidation of dithionic acid by strong oxidizing agents such as dichromate or bromate is the same as its rate of hydrolysis

into sulphuric and sulphurous acids:



In other words, the oxidizing agents have no direct effect on the dithionate ion but merely oxidize the sulphurous acid formed by hydrolysis. The rate of hydrolysis increases with temperature, dithionate concentration, and hydrogen-ion concentration, and is negligible at room temperature. In the present investigation only 0.1 per cent of the dithionate was decomposed when a solution containing 174 grams of calcium dithionate per liter, and having an initial pH of 5.0, was boiled under a reflux condenser for 12 hr.; the final pH was 3.5. In the semipilot plant work described later, solutions containing 100 to 200 grams of calcium dithionate per liter at a pH of about 8 were regularly evaporated to 200 to 300 grams per liter with no detectable decomposition.

Little is known about the mechanism by which SO_2 is oxidized to sulphate and dithionate by MnO_2 or by oxygen. The amount of dithionate formed by reaction 4 is probably negligible, since Bassett and Henry³ have shown that under the most favorable conditions only about 6 per cent of the SO_2 oxidized by oxygen is converted to dithionate, the remainder forming sulphate. The formation of manganese sulphate by reaction 1 is evidently not an intermediate step in the oxidation of SO_2 to dithionate by MnO_2 , since no manganese dithionate is formed when SO_2 is passed through a solution of manganese sulphate. On the other hand, it does not appear that dithionate is formed first by reaction 2 and then oxidized to sulphate by oxygen or MnO_2 , since no sulphate is formed when oxygen is passed through a solution of manganese dithionate, and no manganese is dissolved when manganese dioxide ore is left in contact with dithionate solution in the absence of SO_2 .

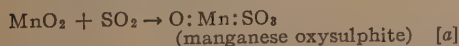
As is shown later, conditions that tend to increase the rate of dissolution of oxygen

relative to that of SO_2 increase the quantity of acid formed by reaction 3, as would be expected. However, such conditions also increase the quantity of manganese sulphate formed and correspondingly decrease the quantity of manganese dithionate formed, whereas reactions 1 and 2 give no indication that oxygen should affect the relative proportions of the products. The effect of oxygen can perhaps be explained by postulating the formation of an intermediate compound that can react either with SO_2 to form manganese dithionate or with oxygen to form another compound that breaks down into manganese sulphate and oxygen.* The relative amounts of manganese sulphate and manganese dithionate formed would then depend on the relative rates of reaction of the intermediate compound with SO_2 and oxygen.

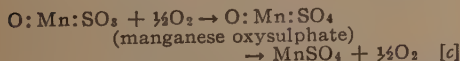
ADVANTAGES AND DISADVANTAGES OF THE DITHIONATE PROCESS

The sulphur dioxide process for manganese ores that has received most attention involves leaching a suspension of the ore in water with sulphur dioxide, recovering manganese sulphate crystals from the solution by evaporation, decomposing the crystals thermally at about 1000°C . into manganese oxide and $\text{SO}_2\text{-SO}_3$ gases, nodulizing the oxide, and recycling the gases to the leach.⁵ This process, which was recently applied on an industrial scale,⁶ requires expensive evaporation and decomposition equipment, as well as

* Such a mechanism is illustrated by the following hypothetical reactions:



or



It is interesting to note that manganese oxysulphate has been isolated.⁴ It decomposes upon contact with water into manganese sulphate and oxygen, as indicated.

large quantities of heat. The dithionate process, on the other hand, utilizes a simple lime-precipitation step in place of the recovery and decomposition of manganese sulphate. It requires, however, slightly more than a pound of lime per pound of manganese recovered, and the sulphur dioxide consumed cannot feasibly be regenerated. A cheap source of sulphur dioxide, such as waste smelter gas, is therefore necessary.

EXPERIMENTAL METHODS AND RESULTS

The dithionate process was first investigated in small-scale laboratory tests, then in a small batch plant in which 50 to 75 lb. of ore was treated per batch, and finally in a semipilot plant in which about 400 lb. of ore was treated per 24 hours.

Laboratory Tests

Laboratory tests on a large number of oxide ores showed that there is no essential difference in manganese extraction whether the ore is suspended in water or in an excess of calcium dithionate solution. Most of the ores gave extractions of 90 to 100 per cent, regardless of wide variations in such conditions as method of agitation, size of grind, rate of gas flow or temperature, provided the ore was kept adequately suspended in the slurry and enough SO_2 was supplied.

To determine some of the factors that affect dithionate formation, laboratory tests were made on water suspensions of samples of readily leachable siliceous ores. The results are summarized in Table 1. In each group of tests all conditions except those indicated were kept constant; however, the cell used, the method of agitation, and other operations varied from group to group. In group F the fine bubbles were produced by introducing the gas through two 0.1-in. outlets and the coarse bubbles by introducing the gas through a single 0.25-in. outlet.

The data show that acid formation becomes greater and dithionate formation less as the ratio of oxygen to SO_2 in the gas increases, the depth of slurry through which the gas passes increases, or the bubble size decreases. Since SO_2 is much more readily absorbed by water than is oxygen, these factors would tend to increase the relative rate of dissolution of oxygen to a greater extent than that of SO_2 .

TABLE 1.—*Factors Affecting Dithionate Formation*

Group	SO ₂ in Gas, Per Cent	Diluent	Variable	Composition of Final Solution		pH
				Mn Per Liter, Grams	Total S as S ₂ O ₈ , Per Cent	
			Volume Ratio O ₂ :SO ₂			
A	4.0	Air	5.0	30	26	1.3
	4.0		0.0	30	77	3.1
B	2.8	Air	7.3	48	30	2.1
	5.1		3.9	47	51	3.0
C	2.9	Air, N ₂	7.0	40	7.3	0.8
	2.9		4.0	44	13.5	1.0
	5.5		3.6	48	17.0	1.4
	7.2		2.7	38	31.5	2.1
	28.0		0.54	38	51.0	2.7
			Depth of Slurry, In.			
D	3.1	Air	8.0	44	36	2.0
	3.5		16.0	44	23	1.9
E	3.1	Air	13.5	63	27.5	1.3
	3.1		20.6	46	21.5	0.8
F	3.4	Air	Bubble Size			
	3.4		Coarse	36	46.5	0.75
			Fine	35	29.4	0.6

To determine the effect of particle size on rate of leaching in the presence of an adequate supply of SO_2 , samples of the ore were agitated with water in which was dissolved 2 mols of SO_2 per mol Mn in the ore; i.e., sufficient to form manganese dithionate. With minus 200-mesh ore the extraction of manganese was 97 per cent within 2 min., with $-150 + 200$ -mesh ore it was 80 per cent in 15 min., while with $-20 + 35$ -mesh ore it was 72 per cent in 15 min. Thus the rate of leaching is

governed largely by the particle size when a large supply of SO_2 is present. The effect of particle size when the supply of SO_2 is limited is considered later.

Larger-scale Batch Tests

After interlocked laboratory tests had indicated that the cycle could be repeated indefinitely, similar tests were made on a scale of 50 to 75 lb. per batch. A small plant was set up at the copper smelter of the American Smelting and Refining Co. at Garfield, Utah, utilizing waste converter gas. The gas was taken from the converter flue just beyond the Cottrell precipitators and contained 2.5 to 4 per cent SO_2 , the average being about 3 per cent. It was pumped through a long pipe, in which its temperature dropped to about 40°C., and then through a glass-wool filter and an orifice meter into the leaching cell.

In each test 50 to 75 lb. of minus 20-mesh ore was mixed with 100 to 150 liters of barren solution containing 150 to 200 grams dithionate ion per liter, and the flue gas was introduced into the slurry at the rate of about 25 cu. ft. per min. for 3 to 6 hr. The slurry was then filtered on a pan filter, and the residue was washed three times; the wash solutions were advanced from test to test, the strongest wash filtrate joining the pregnant solution. Lime, slaked in some of the strong precipitate wash filtrate from the preceding test, was added to the pregnant solution to precipitate manganese hydroxide, which was filtered and washed in the same manner as the residue. The resultant filtrate of barren calcium dithionate solution was advanced to the next leaching test.

Thirty-five tests were made in this manner on three readily leachable ores containing 16 to 30 per cent Mn. In most of the tests the slurry depth was about 24 in., and between 1 and 2 lb. of dithionate ion was formed per pound of

manganese extracted. An average of 2.2 lb. of SO_2 , or 60 to 70 per cent of the SO_2 introduced into the cell, was consumed per pound of manganese extracted. The pH at the end of the leach was usually 1.5 to 3. Lime consumption averaged 1.3 lb. of CaO per pound of manganese extracted compared with a theoretical consumption of 1.02 lb., the excess being required to neutralize the free acid formed and to precipitate the small quantities of iron, zinc, and other impurities extracted.

To obtain data on the effect of bubble size, two comparable tests were made in a 2-ft. cylindrical cell agitated by a small spiderlike impeller rotating within a set of baffles near the bottom of the cell. When the gas was introduced through pipes at the periphery of the cell, so that it had little opportunity to come in contact with the impeller, 21.3 per cent of the sulphur in the final solution was present as dithionate and the final pH was 0.9. However, when the gas was introduced through an opening directly beneath the impeller, so that it was sheared into fine bubbles, only 1.6 per cent of the sulphur in the final solution was present as dithionate and the final pH dropped to zero. A series of tests was also made in a gas-agitated cell similar to a Hunt-Forrester flotation machine. The diameter of the openings through which the gas was introduced was varied from $\frac{3}{4}$ to $\frac{3}{16}$ in., the number of openings being increased correspondingly, but no variation in dithionate formation resulted, probably because the smallest openings were still too large for the effect of bubble size to be manifested.

To study the effect of depth of slurry, a series of tests was made in a long vertical 12-in. cylinder in which the slurry was agitated by the gas stream. The results are summarized in Table 2. As in the small-scale tests, less dithionate and more acid were formed as the depth increased, although the effect on dithionate formation

did not appear until the depth exceeded 40 inches.

TABLE 2.—*Effect of Depth of Slurry*

Slurry depth at start, in..	23	40	40	61	61	98
S_2O_3 ion formed per pound	2.3	2.6	2.5	1.0	0.06	0.02
Mn extracted, lb.....	4.9	3.0	1.9	1.4	1.7	1.6
Final pH.....	4.9	3.0	1.9	1.4	1.7	1.6

Grinding the ore to minus 65-mesh instead of minus 20-mesh had little or no effect on the rate of extraction of manganese. Evidently, under the conditions of the tests, the reactions at the solid-liquid interface took place more rapidly than the SO_2 reached the interface by dissolution and diffusion, so that the leaching rate was governed by the rate of supply of SO_2 rather than by the particle size of the ore.

Varying the pulp density from 14 to 30 per cent solids, which caused the manganese concentration of the final solution to vary from 42 to 138 grams per liter, had no significant effect on the results.

A few tests were made on two refractory ores. Under the usual leaching conditions the extraction of manganese was less than 60 per cent. The extraction could be increased to 85 or 90 per cent by raising the temperature, grinding the ore finer, and agitating the slurry more vigorously.

Continuous Semipilot Plant Tests

In view of the encouraging results obtained in the batch tests at the Garfield smelter, a continuous semipilot plant having a capacity of about 400 lb. of ore per 24 hr. was constructed and operated at the Salt Lake City laboratory of the Bureau. The continuous tests are summarized briefly in the following pages.*

The ore was crushed to minus 10-mesh, mixed with barren calcium dithionate solution, and ground to minus 65-mesh in a batch ball mill. The resulting pulp

* More detailed results of the semipilot plant tests on the various ores investigated will be published in another report.

was diluted with calcium dithionate solution to the desired pulp density and fed continuously to the leaching circuit, which comprised three cells in series. At first each cell consisted of an enclosed cylindrical tank, 16 in. inside diameter and 40 in. deep, agitated by a 6-in. ship-type propeller. The slurry overflowed from each tank through a pipe 17 in. above the bottom, the volume below the overflow level being 14 gal., and entered the next tank near the bottom. Later a "dithionate-maker" cell was constructed, consisting of a conical-bottomed tank of similar capacity in which the slurry was agitated by the leaching gas, and the system was so arranged that this cell could be used instead of the first mechanically agitated cell when desired.

The slurry was leached with SO_2 diluted with air to about 3 per cent. The gas entered each cell through a pipe and emerged near the apex of the conical bottom of the dithionate-maker cell and about 2 in. above the bottom of the mechanically agitated cells. The rate of introduction of gas into each of the three cells in the circuit was controlled separately, but the total rate of introduction was kept at about 25 cu. ft. per minute.

From the last leaching cell the slurry flowed into a similar cell, in which it was aerated to remove any unreacted SO_2 . It was then pumped to a neutralizing tank, where slaked lime was added to raise the pH to about 3.5 in order to minimize corrosion in the filter and to precipitate any iron extracted. The neutralized slurry was filtered and washed countercurrently in a four-compartment Moore-type filter* from which the pregnant manganese dithionate solution was pumped to a precipitation tank. The pH was adjusted to about 9 by the addition of slaked lime, and the resulting precipitate

of manganese hydroxide was filtered and washed in a second four-compartment Moore-type filter. Part of the barren calcium dithionate filtrate was used to slake the lime, and the rest was evaporated to the desired concentration and returned to the head of the circuit.

Each test consisted of 100 to 125 hr. of continuous operation, during which about a ton of ore was treated. The pulp density usually was 20 to 25 per cent, and the concentration of SO_2 in the gas 3.2 to 3.4 per cent. A complete inventory of the plant was taken before and after each run, and all materials entering or leaving the system were carefully measured, sampled, and assayed.

About 40 tests were made, mostly on ores assaying 13 to 18 per cent manganese. The concentration of dithionate ion was usually 180 to 200 grams per liter in the feed solution, but rose to 200 to 250 grams per liter in the final slurry, owing partly to dithionate formation but chiefly to evaporation. The temperature was about 40°C. in the first cell as a result of heat of reaction, but dropped to 35°C. in the aeration tank. Manganese extraction was high for all five ores tested, ranging from 85 to 95 per cent and amounting to more than 90 per cent in most of the tests. Two to 4 per cent of the extracted manganese was precipitated in the neutralization step, and 0.6 to 1.5 per cent was lost as soluble manganese in the washed residue, so that the recovery was about 96 per cent of the extraction.

Total loss of dithionate ion in filtering the residue and the manganese hydroxide precipitate was usually 15 to 20 lb. per ton of ore. With each of the five ores tested it was possible to generate more than enough dithionate to make up for this loss. Dithionate formation ranged from 0 to 0.5 lb. per pound of manganese extracted, or 0 to 150 lb. per ton of ore, and was a function of the ore treated, the type of cell used, and the rate of

* This filter was similar in size and construction to that described by A. L. Fox and others.⁷

leaching in the first cell. In several sets of comparable tests, about twice as much dithionate was formed when the first mechanically agitated cell was replaced by the dithionate-maker cell; the propeller of the mechanically agitated cell evidently tended to shear the gas into fine bubbles. The results of tests in which the extraction in the first cell (using the dithionate-maker cell) was varied are summarized in Table 3; all other conditions were kept constant.

quired 1.1 to 1.3 lb. CaO per pound of manganese extracted compared with a theoretical requirement of 1.02. Total CaO requirements for the 13 to 18 per cent ores ranged from 300 to 430 lb. per ton of ore leached.

Several of the ores contained appreciable amounts of zinc and silver and small amounts of copper and lead. A large proportion of the zinc and copper was extracted and came down with the manganese hydroxide precipitate, but none

TABLE 3.—*Effect of Extraction of Manganese in First Cell on Dithionate Formation*

Ore	Tombstone						Salvador					
Manganese extraction in first cell, per cent. . . .	44	45	56	58	66	70	41	62	65	71	82	83
Total dithionate formed, lb. per pound Mn extracted in system.	0.33	0.35	0.26	0.23	0.28	0.47	0.25	0.10	0.00	0.00	0.04	0.00
Dithionate formation, lb. per ton ore leached. .	105	100	91	69	84	147	73	23	0	0	11	0

The data show that the Tombstone ore had a much greater tendency than the Salvador to form dithionate. With the Tombstone ore dithionate formation passed through a minimum and then increased as the percentage of manganese extracted in the first cell was increased, whereas with the Salvador ore dithionate formation fell rapidly to zero.

The amount of SO_2 consumed was 60 to 70 per cent of that introduced into the system and ranged from 1.5 to 2.2 lb. per pound of manganese extracted. The theoretical consumption would be 1.16 lb. per pound of manganese extracted if all the SO_2 formed MnSO_4 ; 2.33 if all the SO_2 formed $\text{Mn}_2\text{S}_2\text{O}_8$; and 1.37 if 0.5 lb. of dithionate ion were formed per pound of manganese extracted.

The final pH of the leach slurry was generally less than one. To bring the pH to approximately 3.5 in the neutralizing tank usually required the addition of 0.2 to 0.4 lb. CaO per pound of manganese extracted, although one of the ores, which contained 17 per cent lime in the form of calcium carbonate, required no neutralization. The precipitation step re-

quired the silver or lead was extracted. The copper can be removed readily from the pregnant solution by precipitation with scrap iron. Encouraging laboratory results have been obtained on recovering zinc from the pregnant solution by adjusting the pH to about 6.9 with lime to precipitate most of the zinc and a small proportion of the manganese, dissolving the precipitate in sulphuric acid, converting the zinc and manganese sulphates to dithionates by treatment with calcium dithionate solution, filtering off the resulting calcium sulphate, and reprecipitating the zinc with lime. Preliminary tests indicate that at least 85 per cent of the zinc can be recovered in this manner as a 60 per cent product (after calcining), with a loss of less than one per cent of the manganese.

None of the silver-bearing ores was directly amenable to cyanidation. Leaching out the manganese, however, appreciably increased extraction of silver by cyanidation, and the leach residues of two of the ores gave very good silver extractions.

The various ores tested contained 2 to 3.5 per cent iron, up to half of which

was extracted in leaching. The iron in the leach solution, however, was almost completely precipitated in the neutralization step, with the result that the iron content of the manganese hydroxide precipitate did not exceed 0.5 per cent. Phosphorus also went out with the leach residue; although some of the ores contained 0.1 or 0.2 per cent phosphorus, the manganese hydroxide precipitate contained only a trace to 0.05 per cent.

The precipitate usually contained about 50 per cent moisture, and after drying at 110°C. assayed 49 to 54 per cent Mn, 5 to 8 per cent CaO, 2 to 3.5 per cent S, 0.5 to 1 per cent SiO₂, and up to 4.5 per cent zinc. A hard, dense sinter was readily produced by double sintering on a small laboratory sintering hearth. Two typical analyses of the precipitate and the resulting

the precipitate with coke at 1300°C. (The relatively low grade of the product in tests 4 and 8 is due partly to contamination caused by partial slagging of the charge by the crucible and partly to

TABLE 4.—*Volatilization of Zinc from Manganese Hydroxide Precipitate*

Test No.	Temperature, Deg. C.	Coke Added, Per Cent	Time, Hr.	Residue Assay, Per Cent	
				Mn	Zn
		0	0	52.4	3.95
1	1125	0	1	57.1	4.2
2	1125	15	1	62.0	3.3
3	1300	0	1	59.6	4.3
4	1300	0	3	56.4	4.2
5	1300	10	1	63.8	0.4
6	1300	10	3	67.4	0.1
7	1300	20	1	58.5	0.05
8	1300	20	3	55.5	<0.05

TABLE 3.—*Typical Analyses of Manganese Precipitate and Sinter*

Material	Analysis, Per Cent						
	Mn	CaO	S	Fe	P	SiO ₂	Zn
A. Precipitate....	50.6	5.8	2.3	0.2	0.03	0.6	4.3
Sinter.....	61.0	7.3	0.06	1.0		0.7	4.4
B. Precipitate....	53.4	5.9	2.6	0.3	0.04	0.7	4.5
Sinter.....	61.2	7.3	0.03	1.0	0.04	0.7	4.6

sinter are shown in Table 3. Except for their zinc content the sinters meet all specifications for ferro-grade manganese. Most of the iron obviously was picked up from the sintering machine. Elimination of sulphur was excellent, but only 10 to 15 per cent of the zinc was eliminated. The addition of salt or calcium chloride to the precipitate before sintering improved the elimination of zinc only slightly.

Samples of precipitate were heated with coke in small clay crucibles. The results are summarized in Table 4. The data show that a product containing 60 per cent or more manganese and 0.1 per cent or less zinc can be produced by heating

the presence of unconsumed coke.) It is probable, therefore, that zinc elimination would be satisfactory under the conditions prevailing in a nodulizing kiln.

SUMMARY

1. The dithionate process involves leaching oxide manganese ore with dilute SO₂ gas in the presence of calcium dithionate solution, recovering the manganese from the resulting pregnant solution by precipitation with slaked lime, and nodulizing or sintering the precipitate. The process has been tested in a small batch plant using waste smelter gas as a source of SO₂ and in a continuous semipilot plant.

2. More than 90 per cent of the manganese was recovered from most of the ores tested.

3. A final product containing more than 60 per cent manganese and meeting ferro-grade specifications could be produced. Although zinc tends to follow the manganese into the precipitate, zinc can be removed from the pregnant solution by selective precipitation or from the man-

ganese precipitate by volatilization during nodulizing.

4. Sufficient dithionate can be formed in the process to make up for losses. Dithionate formation depends upon the ore, the characteristics of the leaching cell, the rate of leaching, and the SO_2 content of the gas.

5. For each pound of manganese extracted, 1.5 to 2.2 lb. of SO_2 and 1.1 to 1.5 lb. of CaO were consumed. The quantity of SO_2 consumed was 60 to 70 per cent of that introduced.

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Concurrent Firing at the Sulphur Bank and Reed Quicksilver Plants

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(New York Meeting, February 1944)

THIS paper will attempt to show how a metallurgical problem at one California quicksilver mine was solved, and how the solution was applied successfully at another mine.

The pronouns "we" and "our," as used below, refer to the Bradley Mining Co. of San Francisco. The term "concurrent firing" for the purpose of this paper can be defined as feeding and firing a rotary kiln at the same end—that is, of course, the upper end. This is as opposed to "countercurrent firing," the orthodox method, in which a kiln is fed at the upper and fired at the lower end. The terms "quicksilver" and "mercury" are used interchangeably.

EARLY REFERENCES

The earliest work on nonferrous metallurgy, we believe, was *The Pirotechnia* of Vannocio Biringuccio,¹ its first edition having been printed in Italy in 1540. Quoting from its chapter entitled "Concerning Quicksilver and Its Ore":

Quicksilver . . . is one of the gods and has divine strength in itself, and also, to the annoyance of the alchemists, it is winged. Hence, when it sees that it is in gravest danger, it loosens itself from . . . every bond . . . and flies away into the heavens, escaping from the hands of those who crucify it. Almost

laughing, it leaves all its adversaries mocked and scorned, with their phials and filters empty . . .

How thorough a job, under certain conditions, it can do of mocking its adversaries and leaving their phials and filters empty, was found out four centuries later at the Sulphur Bank mine, on the east shore of Clear Lake, in Lake County, California. The other mine mentioned in the title is the Reed, in Yolo County, California, 35 miles by road southeast of Sulphur Bank. Reed and Sulphur Bank ranked respectively fifth and seventh in U. S. production in 1943.

The earliest direct reference we can find to furnacing troubles at these mines was by Thomas Egleston in 1890.² Speaking of Sulphur Bank, Egleston says:

Sometimes there is more sulphur than cinnabar in the ore, which is a detriment to both . . . making the sulphur impure, and rendering the cinnabar difficult to work on account of the soot. In some of the early . . . furnaces the accumulation of soot from the excess of sulphur has been known to penetrate as far as the fan blower at the end of the . . . condensers, and completely prevent its revolution. In order to get rid of the inconvenience of this accumulation . . . , as well as to get a commercial value from the sulphur, it (the sulphur) is now separated by steam and sold. It is claimed that the sulphur alone pays all the expenses of . . . the mine. The mine was first worked for sulphur, and the cinnabar it contained was considered to be an inconvenience, and was carefully picked out and thrown away, as its richness and value were not

Manuscript received at the office of the Institute Aug. 3, 1944. Issued as TP 1889 in METALS TECHNOLOGY, December 1945.

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¹ References are at the end of the paper.

known. This ore is now treated (for mercury) . . . but the mine will always be difficult to work, as the ore occurs in the vicinity of boiling mineral springs, which discharge very large quantities of carbonic acid gas.

These springs emerge at 180°F. They have the appearance of boiling because of the gases bubbling up through them. Underground mining in this area was evidently just as difficult in Egleston's

and Jurassic sedimentaries. These sedimentaries resemble oil-and-gas-bearing ground in the Wilbur Springs district, some 20 miles away, in Colusa County.

In Egleston's time, the Knoxville was known as the Redington mine and the Reed as the California. He said:

At Redington metacinnabarite (the dark sulphide of mercury, now commonly called metacinnabar, and) . . . bitumen, both in



FIG. 1.—SULPHUR BANK PLANT.

Coarse ore bin in foreground; kiln building, right center; condensers, center.

day as we found it to be 40 years later, for he continues:

The ore is mined in an open cut, and in several places the lake level has been reached.

We have mined by opencut methods exclusively since early 1932, and in places have reached a depth of 100 ft. below lake level (Fig. 2).

Egleston also visited the Knoxville district, where our Reed mine is operated. The historically more important Knoxville mine is 4 miles from Reed. The ores of these properties are similar, occurring in the contact zone between serpentine

solid and liquid form . . . (were) frequently found in pockets.

This is characteristic of the richer Reed ore, also, some of which carries more than two gallons of oil per ton.

We shall finish with Egleston by quoting from him briefly regarding early furnacing troubles at Reed, or, as he called it, the California works. That was still in 1890, before the time of mechanical furnaces.

The amount of soot collected in the first six condensers is 6 barrels per week . . . The attempt was made to treat the soot in the

arched chamber opposite the fireplace, but . . . the result was the formation of a large quantity of mercuric sulphide, and the attempt was abandoned . . .

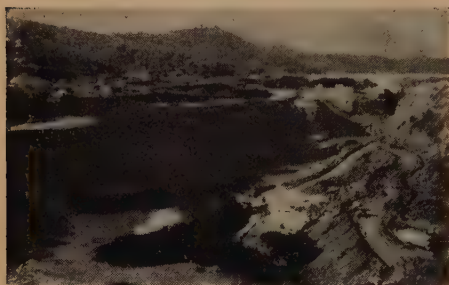


FIG. 2.—HERMAN PIT AT SULPHUR BANK. CLEAR LAKE IN BACKGROUND.

STATEMENT OF PROBLEM

We thus have two mines with many troubles in common. Both went through years of furnacing difficulties because of sulphur in the ore. At the Sulphur Bank the sulphur is predominantly elemental, and runs from 1 to 5 per cent of the furnace feed, depending on whether it is mined from the deeper sedimentaries or the upper, altered basalt. At Reed, although Egleston did not specifically say so, sulphur has also played the role of a damaging impurity. There it is predominantly in the form of pyrite, with additional amounts as elemental and in the oil. We do not know the average sulphur content of the Reed furnace feed, but believe it is considerably higher than that of Sulphur Bank. Samples indicate that the Reed ore runs from 16 to 20 per cent pyrite.

The furnace plants at both mines for years condensed out vast quantities of refractory soot, which contained mercury recombined as a black sulphide, or so finely floured that it would not coalesce. Often it occurred in both conditions. No adequate quantity of free mercury could be worked out by the hand-hoeing methods then in vogue, and it is doubtful whether mechanical hoeing could have

done any better. The material eventually had to be retorted, to secure all the metal.

SULPHUR BANK

Following the success of his first rotary kiln at the New Idria mine, H. W. Gould installed a small rotary kiln at Sulphur Bank, in 1917. It can be taken for granted that this was a countercurrent operation for, as far as we know, there is but one exception to our claim that the only concurrently fed and fired quicksilver kilns ever installed and operated anywhere are the present large ones in use at Sulphur Bank and Reed. The exception is, or was, the 10-ton concurrent rotary plant operated in recent years in El Segundo, Calif., by H. B. Menardi, and described by him in a paper presented at a meeting of the Institute in 1938.³ The Menardi plant treated livingstonite concentrate from Mexico.

An open-cut mining operation supplied ore to Mr. Gould's kiln at Sulphur Bank. He tells us that sorted high-grade went direct to the rotary, and the lower grade, constituting the bulk of the ore mined, went to a concentrating plant. In this plant the ore was screened, crushed, and tumbled, and the table concentrates were added to the kiln feed. However, these concentrates were high in sulphur as well as cinnabar, and the customary soot problems developed in the kiln condensing system. A bank of Johnson-McKay retorts was built below the mill, and a new flowsheet was evolved. The table concentrates went direct to the retorts, together with soot from the kiln operation on high-grade ore.

This operation was short-lived and was followed by a decade barren of any large-scale work at Sulphur Bank. During this period the old brick condensers were picked over for free quicksilver, and an unsuccessful attempt was made to treat the ore by the wet method—that is, by solution in sodium sulphide.

When we entered into our lease at Sulphur Bank in 1927, the firing and condensing problems were given to L. H. Duschak, consulting metallurgist. Dr.

the gases and quenching of the combustion of the sulphur below the possibility of complete oxidation. The mercury vapor and the sulphur vapor combined to form



FIG. 3.

FIG. 3.—BURNER USED AT SULPHUR BANK.

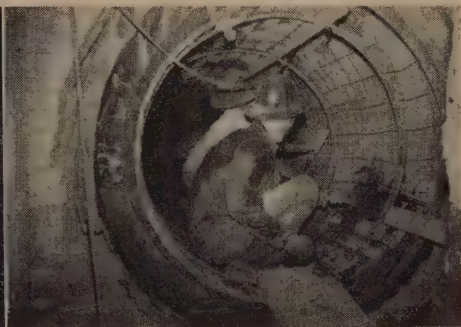


FIG. 4.

FIG. 4.—PLACING REINFORCING WIRE FOR CONCRETE LINING IN KILN AT SULPHUR BANK.



FIG. 5.

FIG. 5.—MECHANICAL HOE (SOOT MIXER) AT SULPHUR BANK.
Liquid mercury flows to bottling room through pipe at left.

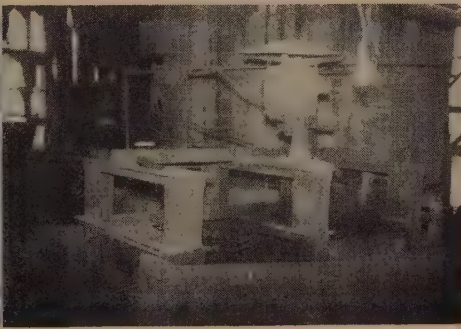


FIG. 6.

FIG. 6.—KRAUT CELL WORKING ON FLOTATION OF MERCURY FROM SOOT, SULPHUR BANK.

Duschak built a small rotary plant and ran tests with it in the laboratory of the Pacific Car and Equipment Co. (now Mutual Engineering Co.), south San Francisco. It soon became apparent that there was not only the sulphur to contend with, but as much as 30 per cent of occluded water. The latter was vaporized near the upper (cold) end of the countercurrently fired test kiln, at or near the same point at which the sulphur was sublimed. The result was reduction of the temperature of

mercuric sulphide, and the condensation of metallic mercury became impossible.

By rearranging the test plant for a concurrent operation, Duschak was able to try out a theory that he had first expressed in 1925.⁵ At that time he had said:

It is possible that more favorable conditions for oxidizing the sulphur in the rotary kiln would follow introducing the fuel at the upper end of the kiln so that the gas stream and the ore moved in the same direction. This scheme would tend to reduce the maximum tempera-

ture of the roasting zone, and at the same time extend it over a considerably greater length of kiln, owing to the heat carried forward by the ore. The thought . . . is that the hot ore



FIG. 7.—PILOT KILN AT REED MINE AS FIRST INSTALLED, WITH COUNTERCURRENT FIRING.

would maintain the furnace gas stream at a temperature above the ignition point of sulphur, clear to the discharge end of the kiln, and also serve as a contact surface for assisting the oxidation of the sulphur vapor. The success . . . would depend upon so aiding the furnace operation that all readily volatilizable sulphur would escape from the ore at some distance from the discharge end of the kiln. The thermal efficiency of a kiln so operated would not be so good as . . . (a) countercurrent (operation) . . . , but . . . should be offset by the heat derived from the oxidation of the sulphur.

Duschak's concurrent operation was successful in test runs on Sulphur Bank ore, and eventually was successful when transplanted to the mine in commercial size in 1927. We say "eventually," because the plant was destined to go through many months of growing pains before the operation was entirely smoothed out.

The plant (Figs. 1, 3-6) built at the mine consisted of a 5 by 60-ft. rotary kiln followed by a rather misfit condensing system. This system was made up of horizontal iron flues, dry and wet electrical precipitation units, a brick spray tower, a wooden tower housing pipe coils through which ran cooling water, and several wood-stave tanks placed vertically and at various angles. The condensing system has under-

gone continuous evolution and every year since 1927 modernization has continued. In fact, only this year a brand new stack and fan unit were added at the end of the system. And no doubt we will continue to replace tile and iron with stainless steel, whenever and wherever possible.

However, awkward as the earlier condensers were, they cannot be entirely blamed for the poor results obtained in this plant in September 1927. Overfeeding of the kiln was the chief deterrent to a successful operation. It was firmly believed by everyone, except by those who had to do the actual operating, that the plant had a capacity of 100 tons per day—so 100 tons per day were put in, whether or not the plant could digest it, and no free quicksilver was produced. Concurrent firing was not getting a fair trial; the burner flame was being partially smothered by a superabundance of wet, sulphurous ore.

The input was gradually and reluctantly reduced, ton by ton and day by day, until a charge of 50 dry tons per day had been reached. At about this point a satisfactory balance was obtained. Quicksilver losses in calcine, waste water, and stack gas reached a relative minimum; total amount of soot caught in the condensers also decreased to a relative minimum; and percentage of free quicksilver in the soot increased to a relative maximum. It must be admitted that enough low-grade soot is still produced, however, to require the constant use of a double-D retort.

From this experience in tonnage, we developed a rule of thumb: A concurrently fired kiln has approximately half the theoretical capacity of a countercurrently fired kiln of the same size. And, conversely, a concurrently fired operation burns twice as many gallons of fuel oil per ton of ore as a countercurrent operation (15.5 and 16.4 gal. per wet ton for Sulphur Bank and Reed, respectively, in 1943). We accepted

these unpleasant facts as necessary adjuncts to the results toward which we were striving; and so, at a later date, when we installed at the Reed mine a kiln rated at

70 per cent of the fuel is burned for the purpose of evaporating this water.

The work required from the condensing plant is proportionately greater because

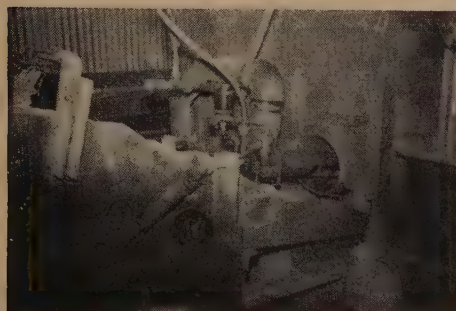


FIG. 8.



FIG. 9.

FIGS. 8 AND 9.—BURNER AND PULSATING FEEDER, REED PLANT.
Fig. 8, side view; Fig. 9, top. Burner is a Mogul, size 19, type SM.



FIG. 10.—REED PLANT NO. 2, COMPLETED IN JANUARY 1942.

a capacity of 80 tons, we did not strain for this figure but were content with the 40-odd tons that eventually were achieved.

To return to the Sulphur Bank kiln: Its shell is 5 by 60 ft., which is somewhat shorter than is the custom today for its diameter, but for Sulphur Bank practice it is probable that an increase in length would not result in greater fuel economy, or much increased capacity.

From September 1927 to Dec. 31, 1943, the water content of Sulphur Bank kiln feed has averaged 21 per cent. This figure sounds more impressive when it is converted into 13.6 tons of water per day, or 543 lb. of water per dry ton of ore. Over

of the high specific heat of the steam and water and the latent heat of the steam. It is estimated that 90 per cent of the work of the condenser is expended on the water alone; consequently, a very large condensing surface is required.

From the dust chamber the gases are drawn through a steel pipe and a standard cyclone dust collector. As these gases are close to a temperature of 1100° to 1200°F. (again, about double that usual in a countercurrent operation), the volume is large and hence the velocity is high. This causes high resistance through the cyclone, and good dust collection.

The body of the condenser plant has been described in other publications. We will go on to the stack; or, rather, to the stack loss. On May 16, 1943, S. H. Williston made a stack determination at Sulphur Bank with his portable ultraviolet appa-



FIG. 11.—CONDENSER PIPES, REED PLANT No. 2.

ratus. The loss was found to be 3.9 lb. of quicksilver per 24 hr., which is not considered unduly high. Average quicksilver recovery at the plant has been 86 per cent from 1927 to the end of 1943. Recovery has improved with practice in recent years, however, and for 1943 was 90 per cent.

In 1931 a patent was granted to us upon the application of L. H. Duschak and the late Clifford G. Dennis. It is entitled "Methods of and Apparatus for Treating Quicksilver Ores," and is made up of four claims. The first three claims

cover in various ways the feature of concurrent firing, or "parallel firing" as it is called in the patent. As for the fourth claim, Duschak wrote of it as follows:

... (It) relates to the method of condensation and covers in a broad way the practice of



FIG. 12.—KILN AT REED PLANT NO. 2.

spraying the hot furnace gases with water and then passing the moisture-laden gases to a separate condenser. On its face, this claim would cover any condenser operation where water sprays are used near the furnace end.

REED MINE

We leased the mineral rights to the Reed mine in 1939, and purchased them outright the following year. In the meantime, we developed enough good ore below the old workings to justify the installation of a small plant. This was a 3 by 36-ft. rotary kiln, followed by vertical cast-iron condenser pipes. It was really a pilot plant, for when work was started in March 1941 the kiln was fired countercurrently (Fig. 7). We thought we should at least make an effort to do things in the orthodox, and theoretically more economical, manner.

Immediate and complete failure to make coherent mercury was the result. The condenser product was a mush of unconsolidated mercury, recombined mercuric sulphide, and unburned oil. The heat (900°F.) produced by the combustion of the fuel oil at the discharge end of the kiln was sufficient to volatilize the mercury from the ore, but the introduction of the

cold ore—with its pyritic sulphur, crude oil, and fairly high moisture content (5 to 10 per cent)—produced a condition that might have been expected. No method

longer requiring a seal (Figs. 8 and 9). At the discharge end, where the firebox had been, and directly above the calcine storage, there was hastily erected a supple-

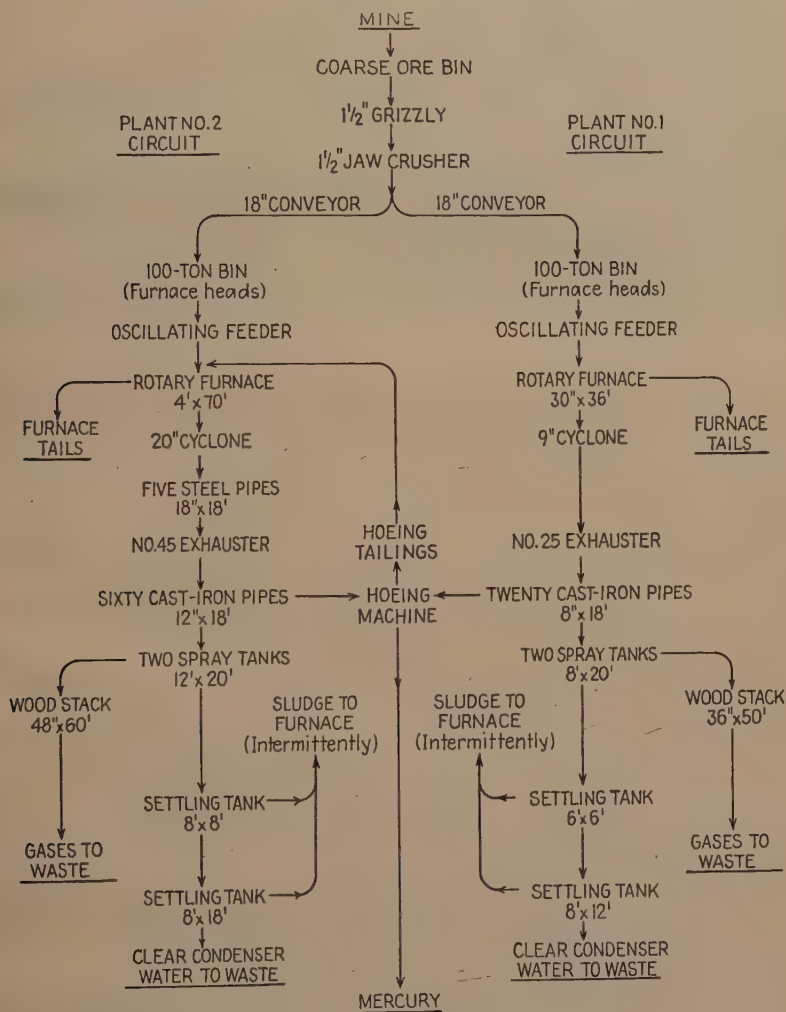


FIG. 13.—FLOWSHEET OF REED PLANT NO. 2.

of air adjustment availed to produce an oxidizing atmosphere throughout the length of the kiln.

The experience at Sulphur Bank naturally suggested concurrent firing at Reed, so the oil burner was moved to the feed end and the pulsating feed pipe was replaced by a pulsating open trough, no

mental combustion chamber with ports for additional air. In two days operations were resumed. The immediate results were liquid mercury from the condensers, in a greatly reduced amount of soot; and a clean stack. Oxidizing conditions obtained throughout the length of the kiln, although by visual observation it was learned that

some of the pyritic sulphur was not consumed until it reached the combustion chamber.

This plant was able to burn only 10



FIG. 14.—COLLECTING SOOT FROM CAST-IRON CONDENSER PIPES.

to 13 dry tons per day and was operating on sorted high-grade. Its best month was December 1941, when it produced 175 flasks from 53-lb. ore. This sort of operation was hardly in the best interests of the mine, however, as it meant that much low-grade ore had to be left underground and in stock piles on the surface. By the summer of 1941 it had been decided to put in a full-sized plant.

Strange as it may seem, there was still doubt as to the proper kind of firing. There was a thought that we had not yet proved that a *large* plant could not be fired counter-currently on Reed ore. So in July 1941 we hauled 100 tons of what we considered typical Reed ore to the plant of our Mt. Diablo mine, in Contra Costa County, California. This plant has a medium-sized kiln—that is, 3 by 40 ft.—fired counter-currently.

After the run of Reed ore, the Superintendent at Mt. Diablo, Phil Cox, reported as follows:

"During the first day's run it was noted that traces of oil floated over the condenser boxes . . . Next morning the temperature at the feed-end header was raised from . . . 900°F. to 1050°F. This eliminated the oil float and tended to drive the silver further down the condenser system . . .

"In washing down the condensers, some

floured quicksilver was observed floating on water surface . . . If this . . . (ore were continued it would) be necessary to inspect condensers at least twice weekly . . .

"Proper settling of the condenser-trough overflow will be important and it will be wise to add aluminum sulphate or the like to improve settling (if all precipitated material is refurnaced or retorted). Considerable soot and . . . cindery material was washed from condensers . . .

"It is our opinion that the Sulphur Bank system of firing . . . will give best results on this material. We believe . . . it is important to obtain maximum combustion as soon as the material enters the kiln. With all the oil and sulphur present in the ore, considerable time is required to complete the burning after ignition . . ."

We considered conclusive this independently arrived at opinion. In addition, we had other evidence, not previously mentioned: In 1940 we had hauled 1600 tons of Reed ore to Sulphur Bank, and we knew that it received successful treatment in that plant.

So we went ahead with plans for a large concurrent plant at Reed. An idle 4 by 60-ft. kiln was secured from the Black Butte mine in Oregon and hauled to Reed, where an additional 10 ft. was riveted to the shell. This made the kiln 4 by 70 ft., longer than standard, in order to insure complete combustion of the pyrite.

The new plant (Fig. 10) complete with condensers (Fig. 11) was put into operation in Feb. 1942. The kiln (Fig. 12) operates with a temperature of 1200° to 1300°F., slightly higher than that at Sulphur Bank. The flowsheet is given in Fig. 13.

The cyclone dust collector following the kiln has an inlet and outlet diameter of 20 in. The large volume of air leaving the furnace makes necessary a larger collector than is customarily used for a kiln of this size.

Following the dust collector, there are enough steel pipes to cool the gases to a temperature of about 500°F. before they enter the fan. At Sulphur Bank the gases

of the gases close to atmospheric. The second is usually run without spray and is intended to provide surfaces to which the finely divided mercury may adhere. The



FIG. 15.

FIG. 15.—LOW-GRADE SOOT MIXED WITH LIME BY HAND SHOVEL.



FIG. 16.

FIG. 16.—SOOT-MIXING MACHINE.

enter an alloy steel (18-8) fan at what may be a temperature of over 1000°F., but at the time the Reed plant was erected alloy steel was no longer available, and it is therefore necessary to cool the gases before they enter the steel-plate fan.

From the fan the gases enter two rows (in parallel) of 12-in. by 18-ft. C.I. pipe condensers, 30 in each row (Fig. 14). These condensers have proved quite efficient in condensation of the mercury, and notwithstanding the high sulphur contents of the gases, only a few of the pipes on the cold end have needed renewal in the two years of operation. A hand crane traveling on an overhead trolley the whole length of the condenser building facilitates the handling of the heavy pipes, and the replacement of a pipe is a matter of only a short time and little labor. The arrangement of these vertical pipes promotes the free circulation of air, and the use of outside water sprays has never been necessary even in the hottest weather.

From the metal condensers, the gases pass through two vertical tanks arranged in series. These are 12 by 20 ft. and are provided inside with horizontal 1 by 4-in. cross slats. The first tank is cooled by a water spray, which brings the temperature

terraced site of the plant permits the drainage from the floor of the condensers, and all the cooling water and floor washings, to be collected in settling tanks.

A test of the gases made during the summer of 1943 showed a stack temperature of 91°F., and the Williston test gave a stack loss of only 3 lb. per day.

The yield of clean metal from the condenser material is high, as the method of firing gives such complete oxidation of the whole contents of the charge that there is no fouling of the metal. The efficiency of the cyclone in the removal of the dust is high and the mechanical "hoe" used on the condenser discharge leaves little residue to be returned. No retort is used. The low-grade soot—that remaining after hoeing, and that collected from runoff water—amounts to only one or two wheel-barrow loads per day, and is dumped into the kiln feeder. (Figs. 15 and 16.)

Quantitative control of plant input is effected by samples of the kiln feed taken every hour. Tonnage is determined by timing and weighing these samples, and the samples are combined every 24 hr. for splitting and assaying. Plant recovery (bottled mercury vs. calculated input) has

averaged 97 per cent. It is thus obviously a more efficient plant than that at Sulphur Bank, its designers having had an opportunity to profit from previous trials and errors.

SUMMARY

The ores of both the Sulphur Bank and Reed mines contain sufficient sulphur, in various forms, to render difficult the condensation of free mercury. The sulphur does not completely oxidize in ordinary countercurrent firing, but recombines with mercury in the condensers and comes down in the soot. A laboratory rotary kiln fired concurrently at 1200°F. indicated that this practice would burn out all the sulphur and allow condensation of free mercury. The principle was applied in the installation and successful operation of a 5 by 60-ft. rotary kiln and condenser plant at Sulphur Bank in 1927. The same principle was used successfully in a 4 by 70-ft. rotary plant at the Reed mine in 1942, after experimentation with a pilot plant in 1941.

ACKNOWLEDGMENTS

Valuable assistance in the preparation of this paper was given by the two superin-

tendents, A. F. Wolbert, of Sulphur Bank, and C. T. Boyd, of Reed.

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Treatment of Idaho-Wyoming Vanadiferous Shales

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(New York Meeting, March 1947)

THE vanadiferous shales of southeastern Idaho and southwestern Wyoming constitute the largest known reserve of vanadium in the United States.¹ These deposits have never been exploited except for the relatively small amounts of vanadium recovered by the Anaconda Copper Mining Co. in the treatment of phosphate rock from southeastern Idaho. The major domestic source of vanadium has been the sandstone ores of southeastern Utah and southwestern Colorado.

Early in World War II, it appeared that these ores could not meet the greatly increased demand for vanadium, so the investigation described in this report was undertaken to develop processes for the recovery of vanadium from the Idaho-Wyoming deposits. The utilization of these deposits became unnecessary, however, because of greatly expanded production from the Utah-Colorado sandstone ores and the continued availability of vanadium from other sources, chiefly Peru.

The major use of vanadium is as an alloying agent in the manufacture of high-quality steels. Vanadium constructional

steels usually contain 0.05 to 0.20 pct vanadium, which refines the grain and increases the strength, elastic limit, and resistance to shock and fatigue. Vanadium tool steels not used in high-speed work contain 0.10 to 0.60 pct whereas high-speed tool steels contain 1.0 to 4.0 pct. Vanadium compounds are used as catalysts (principally for the oxidation of SO₂ to sulphuric acid and of naphthalene to phthalic acid) and in the paint, chemical, ceramic, dye, and printing industries.

The selection of the particular ore deposit to be exploited would involve consideration of many factors besides the metallurgical results that might be obtained. Chief among these would be the reserves of ore available, the grade of the ore, and the mining costs. As very little was known about any of these factors, it was necessary to investigate methods of treatment of all the ores under consideration, working with samples obtained in the course of the exploration work, even though they were not positively representative of the whole deposit from which they were taken. Because of wartime conditions prevailing when this investigation was started, first consideration was given to processes that could be put into operation most quickly and would involve minimum use of strategic materials, even though these processes might not be the most economical.

Published by permission of the Director, Bureau of Mines, U. S. Department of the Interior. Manuscript received at the office of the Institute Dec. 30, 1946. Issued as TP 2178 in METALS TECHNOLOGY, June 1947.

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¹ References are at the end of the paper.

ACKNOWLEDGMENTS

The investigation of the Idaho-Wyoming vanadiferous shales was suggested by R. S. Dean, former Assistant Director of the Bureau of Mines, and was carried out under the general supervision of S. R. Zimmerley, chief of the Salt Lake City Division, Metallurgical Branch. Ore-dressing tests were made by the Ore Dressing Section of the Salt Lake City station

engineer of the Metals Reserve Co., for helpful suggestions and assistance in arranging for close coordination between the exploration work and the metallurgical work.

ORES INVESTIGATED

Three major deposits were selected for exploration and metallurgical investigation, and samples were taken from each deposit as exploration work progressed.

TABLE 1—*Analyses of Vanadiferous Shales and Phosphate Rock*
PER CENT

Deposit	Lot No.	V ₂ O ₅	P ₂ O ₅	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	CaO	S	CO ₂	Organic C	MoO ₃	TiO ₂	Loss on ignition	F
Sublette Ridge....	I-2	0.65	2.9	52.3	3.9	9.5	7.1			3.9	0.01	0.9	11.6	
	I-3	0.52	2.6	43.8	4.0	12.7	9.9	4.1	6.5	10.7	0.02	0.7		
	I-4	0.77	0.9	46.5	4.2	12.2	6.5	4.1	5.8	10.9	0.02	0.7		
	I-9	0.53	2.1	42.2	3.4	11.6	10.4	3.4	6.2	9.2	0.01	0.7		
	I-10	0.92	0.8	49.0	3.9	12.7	5.2	4.0	4.6	8.5	0.02		19.5	
	6-5	0.74	1.4	44.0	3.6	10.9	7.8	4.0	4.7	4.7	0.02		20.3	
	I-5	0.93	2.8	43.3	4.1	10.3	8.4	4.0	5.2	10.1	0.02			
	I-6	1.98	0.2	42.1	4.0	12.1	4.6	5.9	3.5	15.2	0.05			
	I-7	1.34	0.5	46.8	3.9	12.2	4.9	4.6	4.0	10.7	0.03			
	I-8	1.32	0.6	44.7	3.4	12.1	5.8	4.7	4.1	9.9	0.03		21.9	
Dry Creek.....	I-11	1.07	4.0	40.0	3.6	7.1	8.8	3.3	4.4	12.7	0.07	0.4	20.7	
	6-2	0.75	1.6	54.8	3.9	12.6	3.5	0.5	0.2	4.2	<0.01		13.0	
	6-3	0.50	21.9	23.0	2.2	11.5	15.8	0.2	0.6	3.1	<0.01		8.6	
	6-4	1.16	11.8	24.9	2.1	12.2	15.2	1.6	0.6	11.7	<0.01		25.9	
	6-6	0.91	11.3	23.8	2.2	10.1	13.8	3.2	3.2	17.1	0.02	0.3	27.7	
	6-7	0.91	10.7	25.4	2.0	11.2	12.0	4.2	1.7	10.1	0.08		28.7	
	6-8	1.35	10.4	16.6	2.6	9.3	10.5	5.8	0.5	16.2	0.08		40.6	
	6-9	1.08	9.8	23.4	2.7	12.3	11.8	3.9	1.5	9.7	0.07		32.1	
	6-10	1.17	10.3	30.2	3.0	11.1	12.6	2.0	0.6	12.6	0.02	0.3	24.8	
	6-11	0.86	3.0	45.4	1.7	10.2	3.6	2.1	0.4	14.4	0.02	0.6	27.7	
Siltstone.....	6-12	0.49	22.8	16.8	2.3	4.3	30.2	1.2	0.7	8.5	<0.01	0.2	16.2	
Oolite.....	6-13	1.60	12.8	15.0	1.4	4.7	17.4	4.6	0.6	25.7	0.07	0.2	41.2	
Shale.....		0.94	13.1	23.4	1.8	6.8	17.4	2.8	0.6	16.0	0.03		30.0	0.3
Paris composite..	6-15	0.69	10.2	18.4	1.8	3.7	25.0	3.4	4.6	18.8	0.07	0.3	28.7	0.2
Phosphate rock...	6-14	0.14	32.7	6.8	0.9	1.1	49.2	0.6	1.7	0.5	<0.01	<0.01	7.0	2.6

under the direction of H. G. Poole. A. L. Fox, W. M. Sternberg, B. J. Kerley, A. E. Back, and K. E. Tame participated in the early part of the hydrometallurgical work and made valuable contributions.

The authors wish also to express their appreciation to J. D. Johnson, manager of the Sublette Division of the Wyodak Coal and Manufacturing Co., which, as agent for the Metals Reserve Co., provided the various samples of ore used in this investigation; to H. A. Walker, assistant general manager, and Nathaniel Herz, chief metallurgist, Wyodak Coal and Manufacturing Co., for their cooperation; and to S. Power Warren, metallurgical

Analyses of a number of the samples are summarized in Table 1.

The mineralogical occurrence of the vanadium is not known, despite a great deal of microscopic examination, which included examination with the electronic microscope by the National Bureau of Standards. The microscopic results, together with the negative results obtained in all attempts at concentration by ore-dressing methods, indicate that the vanadium is very finely disseminated through the shale.

The location and description of each of the three deposits follows.

Sublette Ridge Deposit—The Sublette

Ridge deposit is in the Evans, Coal, and Raymond Canyons area of Sublette Ridge, Lincoln County, Wyo. The ore consists of a fairly soft, fine-grained, black, carbonaceous shale. The beds are composed of layers that are alternately rich and lean in vanadium, the high-vanadium layers being richer in organic matter. Unlike the Colorado-Utah ores, the Sublette Ridge ore is relatively high in acid-soluble iron and aluminum and contains nearly 10 pct organic carbon and 1 to 3 pct P_2O_5 .

Salt River Range Deposits—The area of the Salt River range that has been examined most intensively is the Dry Creek canyon deposit about 6 miles southeast of Afton, Lincoln County, Wyo. Preliminary exploration indicates that the ore is of slightly better grade than that from Sublette Ridge and that the beds are more continuous. Like the Sublette Ridge ore, the Dry Creek ore is a layered, black, carbonaceous shale containing considerable amounts of acid-soluble iron and aluminum, some phosphate, and 10 to 15 pct organic carbon.

Paris-Bloomington Deposit—The Paris-Bloomington deposit is in Bear Lake County, Idaho; it outcrops in Paris and Bloomington canyons near the towns of the same names. The vanadiferous zone consists of adjacent beds of clayey shale, oölite, and siltstone, each approximately 3 ft wide. The ore differs from the Sublette Ridge and Dry Creek ores in that it contains an average of 10 pct P_2O_5 .

Lots 6-6 and 6-10, Table 1, are samples from the weathered-ore zone of the Paris deposit; lots 6-11, 6-12, and 6-13 are 1-ton samples of each of the adjacent layers from the unweathered zone; "Paris composite" represents a composite of lots 6-11, 6-12, and 6-13; lot 6-15 is an 8.5-ton sample from the Metals Reserve Co. stock pile in Paris canyon; and lot 6-14 is a sample of high-grade phosphate rock from Bloomington canyon.

VANADIUM TECHNOLOGY

Specifications for Vanadium Pentoxide

No formal specifications have been established in the industry for vanadium pentoxide, but trade practices usually demand a minimum of 85 pct V_2O_5 . The permissible contents of phosphorus, sulphur, and copper are established indirectly through the ferrovanadium specifications of the U.S. Metals Reserve Co., as it is probable that most of these impurities present in the vanadium pentoxide will be carried over into the ferrovanadium. Table 2 gives the Metals Reserve Company's specifications for two grades of ferrovanadium. On the basis of these

TABLE 2—*Metals Reserve Company Specifications for Ferrovanadium*
PER CENT

Constituent	Open-hearth Grade	Special Grade
Vanadium.....	50-55	50-55
Carbon.....	3.00 max	1.00 max
Silicon.....	8.00 max	4.00 max
Sulphur.....	0.20 max	0.15 max
Phosphorus.....	0.20 max	0.15 max
Aluminum.....	1.50 max	1.50 max
Copper.....	2.00 max	1.00 max

specifications the maximum permissible phosphorus or sulphur content of an 85-pct V_2O_5 product would be about 0.2 pct for open-hearth grade ferrovanadium and 0.15 pct for special grade if the phosphorus or sulphur content of the iron used in making the ferrovanadium is neglected, or about 0.17 pct and 0.12 pct, respectively, if it is assumed that the iron contains 0.05 pct each of phosphorus and sulphur.

Standard Treatment of Colorado-Utah Ores

The process^{2,3} employed for commercial treatment of the Colorado-Utah sandstone ores varies somewhat with the ore being treated. In general, however, the ground ore is roasted with salt (and sometimes pyrite) at 800° to 900°C under oxidizing conditions, to convert the vana-

dium to soluble sodium vanadate. The sodium vanadate is extracted by leaching with hot water or soda-ash solution, the solution is oxidized with sodium chlorate if necessary, sulphuric acid is added to lower the pH to about 3, and the vanadium is precipitated as "red cake" by prolonged agitation at 80° to 95°C. The precipitate, which contains 80 to 90 pct V_2O_5 , is filtered, washed, dried, and fused at a temperature of 870° to 925°C. The fused product is known as "black cake" and usually contains about 90 pct V_2O_5 . It is understood that over-all recovery of vanadium is usually 70 to 80 pct.

Calcium in the form of carbonate tends to form insoluble calcium vanadate in the roasting process and thereby interferes with the formation of water-soluble vanadium. If the ore contains more than about 1.8 parts $CaCO_3$ to 1 part V_2O_5 , pyrite is added to minimize the formation of calcium vanadate by converting part of the lime to calcium sulphate. Excessive roasting temperatures lower the extraction of vanadium, probably owing to silicate formation.

Red Cake—In the precipitation of red cake, poly-acids of vanadium, the composition of which depends largely upon the pH, apparently are formed by hydrolysis of the sodium vanadate; upon prolonged heating and agitation, the poly-acids polymerize to colloidal particles, which then slowly agglomerate and precipitate.⁴ The chemical formula of the precipitate has been given as $Na_2H_2V_6O_{17}$.² Fusion of the red cake to black cake eliminates moisture, both free and combined, and a large part of the sulphur (particularly if the sulphur content is high) but does not otherwise alter the composition.

Anaconda Process for Recovery of Vanadium from Phosphate Rock

At the phosphate fertilizer plant of the Anaconda Copper Mining Co. at Anaconda,

Mont., V_2O_5 is recovered as a by-product in the production of treble superphosphate. The phosphate rock, which is mined at Conda in southeastern Idaho, contains approximately 0.3 pct V_2O_5 . The process used is described as follows:⁵

The rock is treated with sulphuric acid, primarily for the purpose of leaching out the phosphoric acid. At the same time, approximately 65 pct of the vanadium contained in the rock goes into solution together with the phosphoric acid. This is precipitated as phospho-vanadic acid by treating the solution with sodium chlorate. The yellow crystalline precipitate is separated by settlement.

It contains phosphorus, iron, alumina, lime, and other impurities. By treatment with milk of lime and soda ash under carefully controlled conditions, the vanadium is obtained in a substantially pure sodium vanadate solution, from which vanadium pentoxide, V_2O_5 , is precipitated by the addition of sulphuric acid. This is the 'red cake' precipitate, which, upon drying, is ready for market.

The strong phosphoric acid from which the phosphovanadic acid has been precipitated is treated with calcined rock to form treble superphosphate.

Phosphovanadic Acid—As indicated above, when a strong phosphoric acid solution containing vanadium is oxidized, the vanadium precipitates out as yellow phosphovanadic acid (also known as phosphatovanadic acid). The general formula for phosphovanadic acids is $V_2O_5 \cdot P_2O_5 \cdot nH_2O$,^{6,7} where n usually is 3 or 4, but the product actually obtained varies somewhat from this formula, depending upon the concentration of the solution, the impurities present in the solution, the temperature of precipitation, and the oxidizing agent used. The recovery of phosphovanadic acid from phosphoric acid solutions has been patented by Bowman,⁶ and the Anaconda method of recovering V_2O_5 from the phosphovanadic acid has been patented by Frick and Woodman.

APPLICATION OF STANDARD ROAST-LEACH PROCEDURE TO IDAHO-WYOMING SHALES

The first test work on each of the ores was a study of the salt-pyrite roast method, with the object of making as much as possible of the vanadium water-soluble, so that it could be recovered as commercial-grade V_2O_5 by the usual red-cake precipitation procedure. It was felt that the simplicity of this method might compensate for low recoveries and permit plant operations to get under way, if necessary, with a minimum expenditure of time and equipment.

A number of tests were made in which the roasted product was leached with 2 pct sodium carbonate solution or with 1 or 2 pct sulphuric acid solution. In general, the sodium carbonate solution extracted 5 to 10 pct more vanadium than the simple water leach and the dilute acid extracted 10 to 20 pct more, but the resulting solutions were high in phosphorus. For example, an ore having a ratio of P_2O_5 to V_2O_5 of about 3 gave, after being roasted with salt and pyrite, a sodium carbonate extraction having a ratio of one and a sulphuric acid extraction having a ratio of 5, whereas the water extraction contained virtually no phosphorus.

In addition to salt-pyrite roasts, roasting tests were made with many other reagents, including NaF , Na_3PO_4 , Na_2SO_4 , K_2SO_4 , H_2SO_4 , $Na_2B_4O_7$, Na_2CO_3 , K_2CO_3 , $NaOH$, KOH , Na_2S , $NaNO_3$, and various mixtures of these. With one exception, the highest water extractions were obtained with salt and pyrite. A slightly higher extraction was obtained after roasting the ore with a mixture of 5 pct KOH and 2 pct $NaNO_3$ (based on the weight of ore), but the resulting solution contained excessive amounts of impurities.

Sublette Ridge Ore

An extensive series of tests was made on Sublette Ridge ore 1-10 (Table 1) to

determine the optimum conditions for the salt-pyrite roast. For these tests 500-gram samples were rabbled by hand on the hearth of a gas-fired laboratory muffle furnace. No appreciable water-solubilization of the vanadium took place until the carbonaceous material in the ore had been virtually burned off. For this reason the procedure was adopted of calcining the ore at $750^\circ C$ and then adding the reagents and roasting again at the desired temperature. The best water extraction (50 pct) was obtained by roasting the calcined ore with 3 pct pyrite and 18 pct salt (based on the weight of raw ore) for 2 hr at $900^\circ C$. Longer roasting or higher temperature caused a decrease in extraction, probably because of the formation of silicate. Substantially the same extraction was obtained with minus 10 or 20-mesh ore as with minus 100-mesh ore.

A strongly oxidizing atmosphere during the roasting was found to be important; for example, in a series of comparable tests in which raw ore was roasted with 3 pct pyrite and 18 pct salt at $900^\circ C$ and then leached with cold 1 pct sulphuric acid solution, maximum extraction of vanadium was 31.5 pct with furnace door and flue damper closed, 61.1 pct with flue damper open, and 79.6 pct with flue damper open and door partly open. Similarly, extraction decreased as the depth of the ore bed increased.

A number of tests were also made on 50-lb samples of ore in a small rotary kiln, 3 pct of pyrite and 18 pct of salt being added after the ore had been calcined. The maximum water extraction (52 pct) was obtained at $900^\circ C$. The 7 pct decrease in extraction as compared with the results in the muffle furnace is due probably to the less effective rabbling in the rotary kiln.

By acid hydrolysis of the various water extractions, 98 pct of the dissolved vanadium was precipitated as red cake assaying 80 to 88 pct V_2O_5 , about 3 pct

MoO₃, less than 0.02 pct P, and 0.04 to 3 pct S. The sulphur was present as calcium sulphate, and subsequent work has shown that it can virtually be eliminated by treating the water extractions with a small quantity of sodium carbonate and filtering off the precipitate of calcium carbonate before adding the acid.

Dry Creek Ore

Under conditions similar to those described for Sublette Ridge ore, Dry Creek ore 1-8 (Table 1) gave maximum water extractions of 66.4 pct in muffle-furnace tests and 56.1 pct in the rotary kiln.

Paris-Bloomington Ore

There was considerable difference in behavior among the various samples of Paris-Bloomington ore. With lot 6-10, the mixture of 18 pct salt and 3 pct pyrite found most favorable for the Sublette Ridge and Dry Creek ores made only 5 pct of the vanadium water-soluble; little improvement was gained by varying the temperature or the proportions of salt and pyrite. It was found, however, that adding the salt as brine instead of in the solid state gave much better results. The highest water extraction (56.4 pct) was obtained by roasting calcined ore in the muffle furnace with 4 pct salt (as brine) and 6 pct pyrite at 750°C for 2.5 hr. These results point to the possibility that higher extractions might have been obtained from the Sublette Ridge and Dry Creek ores if the salt had been added as brine.

The highest solubilization of vanadium obtained for any of the shale samples was with the Paris composite, which gave a water extraction of 71.2 pct after the calcine was roasted in the muffle furnace with 9 pct salt (as brine), but no pyrite, for 2.5 hr at 750°C.

On the other hand, lot 6-15 was completely unamenable to water-solubilization of vanadium, probably because of its

high CaCO₃ content. The highest extraction obtained was 1.5 pct, despite extensive testing with a wide variety of reagents at various temperatures and roasting periods.

ACID PROCESSES FOR SUBLETTE RIDGE AND DRY CREEK ORES

Because of the rather low extractions obtained from the Sublette Ridge and Dry Creek ores by the salt-pyrite roast method, other methods of recovering the vanadium were investigated. A series of acid leaches at the boiling point was made on Sublette Ridge sample 1-10, using different acids and 10-gram samples of raw ore and ore calcined at 500°C. The results are summarized in Table 3.

TABLE 3—*Acid Leach of Raw and Calcined Ore, Sample 1-10*

Charge	Leach Solution, Parts by Volume		V ₂ O ₅ Extraction, Pct
	Water	Acid	
Raw.....	1	H ₂ SO ₄ -1	54
Raw.....	1	HNO ₃ -1	58
Raw.....	1	HCl-1	25
Raw.....	5	Aqua regia-1	63.5
Raw.....	5	H ₂ SO ₄ -4, HNO ₃ -1	80.5
Raw.....	5	H ₂ SO ₄ -4, HCl-1	64.0
Calcined..	1	H ₂ SO ₄ -1	91.9
Calcined..	1	HNO ₃ -1	51.4
Calcined..	1	HCl-1	59.0
Calcined..	1	Aqua regia-1	69.1
Calcined..	5	H ₂ SO ₄ -4, HNO ₃ -1	86.0

The data show that the calcined ore was more amenable to leaching than the raw ore and that sulphuric acid was the most effective leaching agent for the calcined ore. The most favorable calcining temperature was 500°C. Salt and pyrite in the charge during calcination did not improve the extraction of vanadium. The extraction in 50-vol pct nitric acid could be increased to 96 pct by leaching the calcine in an autoclave at 150° to 175°C. However, nitric acid leaching appeared to have no particular advantages, so further work was done with sulphuric

acid, as a result of which the leach-bake and acid-bake processes were developed.

Leach-bake Procedure

The leach-bake process was carried out as follows: 250 grams of calcine was leached for 20 min. at 175°C with 300 ml of 70 pct (by weight) sulphuric acid solution, and the slurry was filtered but not washed. The filtrate was made up to original volume with about 175 ml of 70 pct acid and used on a fresh batch of calcine, and the process was continued for 16 cycles. Filtering rates were reasonably good, provided the slurry was cooled to room temperature to avoid crystallization of sulphates in the pores of the filter cloth. Each filter cake was baked at 300° to 400°C to volatilize the free sulphuric acid, which would be recovered in practice. To extract the vanadium, the baked cake was leached counter-currently with the filtrate from the first vanadium precipitation described below, make-up water being added in the final wash. The iron, aluminum, and magnesium sulphates extracted during the leach eventually left the system in the washed filter cake, since after a few cycles all the wash filtrates became saturated with sulphates. Vanadium extraction for the 16 cycles ranged from 84.7 to 97.5 pct, averaging 93.6 pct and showing no trend. The pregnant solution averaged 9 grams per liter V_2O_5 and 0.4 pH.

By agitating the pregnant solution for about an hour at 90°C with sufficient sodium carbonate to raise the pH to 1.5, approximately 75 pct of the vanadium was precipitated; the product contained 36 to 48 pct V_2O_5 , a typical analysis being 46.4 pct V_2O_5 , 1.8 P_2O_5 , 13.5 Al_2O_3 , 21.7 Fe_2O_3 , 11.8 TiO_2 , 0.4 MgO , less than 0.1 CaO , and 2.8 MoO_3 . The precipitate was redissolved in sodium hydroxide solution, the alumina and most of the phosphorus and titanium were dropped out with virtually no loss of vanadium

by adjusting the pH to 8.0 to 8.5 with carbon dioxide, and the vanadium was reprecipitated from the purified solution by acid hydrolysis. The resulting red cake assayed approximately 85 pct V_2O_5 and contained no phosphorus.

Acid-bake Procedure

The acid-bake procedure is a modification of the leach-bake process just described. Calcine in 5-lb batches was mixed with 36 pct by weight of sulphuric acid added as a 67 vol pct solution. The mixture was baked for 30 min. at 175°C and leached with water; 93 pct of the vanadium was extracted. The baked product and the leach solution were then treated as in the leach-bake procedure, with similar results.

This procedure probably is preferable to the leach-bake procedure. It seems well suited for large-scale continuous operation, since the calcine-acid mixture is dry enough to permit good rabbling in a multiple-hearth furnace. The quantity of acid used corresponded to 43 lb H_2SO_4 per pound of V_2O_5 recovered, but a substantial part of this might be recovered if the baking were done at a higher temperature.

PVA ORE-ROAST PROCESS

Paris-Bloomington Ore

The Paris-Bloomington ores contain an average of 10 pct P_2O_5 (Table 1), so that serious consideration must be given to recovery of phosphate, as well as vanadium, in marketable form. Since the simple roast-leach process gives rather poor recovery of vanadium and does not extract phosphate, considerable work was done on the use of sulphuric acid to recover phosphate and improve the recovery of vanadium. All the methods investigated involved the formation of phosphovanadic acid (hereinafter referred to as PVA), as in the Anaconda process.

During the investigation of lot 6-10 (Table 1) it was found that when PVA is mixed with the ore and the mixture is roasted with salt, a water leach of the roasted product extracts not only the usual quantity of vanadium from the ore but also all the vanadium from the PVA, whereas virtually none of the phosphorus is extracted. This led to the development of a relatively simple process in which the ore is roasted with salt and leached with water, the water-leach residue is leached with sulphuric acid, the acid-leach solution is concentrated by evaporation and oxidized with sodium chlorate to precipitate PVA, and the PVA is recycled to the roasting furnace with the next batch of ore. The vanadium is recovered from the water-leach solution as red cake by acid hydrolysis, and the PVA filtrate, consisting principally of phosphoric acid solution, is used for the production of phosphate fertilizer.

A series of five interlocked cyclic tests was made in which the unwashed PVA was mixed with minus 40-mesh raw ore 6-10 and the mixture was roasted with 6 pct of salt (based on the weight of ore) added as brine. An over-all average of 87.6 pct of the vanadium in the ore was extracted by leaching the roasted product with water, 50 to 55 pct being extracted directly from the ore and the remainder from the recycled PVA. The residue was leached with 53 pct sulphuric acid solution, using 600 lb H_2SO_4 per ton of ore, and the acid-leach residue was washed counter-currently; the average extraction of P_2O_5 was 83.3 pct. The acid-leach liquor was evaporated to a specific gravity of 1.65, oxidized with sodium chlorate, and allowed to stand for 6 to 24 hr. The PVA was then filtered off and recycled to the roast. The PVA filtrate contained less than 2 pct of the total vanadium. Tests with minus 20-mesh ore gave approximately the same recovery of vanadium but a considerably lower extraction of phosphate.

Similar interlocked tests on the composite ore (Table 1), using 9 pct salt (4 pct as brine and 5 pct dry) in the roast and 800 lb H_2SO_4 per ton of ore in the acid leach, gave average extractions of 90.8 pct of the vanadium and 81.9 pct of the phosphate. When the acid solution was added to the water-leach residue, the slurry tended to gel, but this difficulty was overcome by adding the residue slowly to the acid solution. By drying the water-leach residue, pugging it with concentrated H_2SO_4 , repulping with water, filtering, and washing the resulting residue with dilute acid, 91.5 pct of the vanadium and 90.0 pct of the P_2O_5 were extracted in 13 cycles; with a consumption of 750 lb H_2SO_4 per ton of ore.

In the various cyclic tests on lot 6-10 and on the composite, the water-leach solutions usually contained 20 to 25 grams of V_2O_5 and 0.1 to 0.3 grams of P_2O_5 per liter. Red cake was readily precipitated from such solutions, and the black cake, produced by fusing the red cake, assayed 85 to 93 pct V_2O_5 and less than 0.05 pct P or S.

Lot 6-15 (Table 1) behaved quite differently from lot 6-10 or the composite sample. As mentioned previously, it is not amenable to the simple roast-leach process. Moreover, when PVA was roasted with the ore, the vanadium in the PVA could not be made water-soluble despite considerable testing with salt, pyrite, and other reagents under various conditions of time and temperature.

Dry Creek Ore

The maximum extraction of vanadium from Dry Creek ore by the simple roast-leach process was 66 pct. Tests were made therefore by the PVA ore-roast process, using phosphate rock to provide phosphate for the formation of PVA. A series of eight interlocked tests was made on 1000-gram batches of ore 1-11 as follows: The raw ore was roasted at 750°C

with 8 pct of salt and leached with water. The residue was leached with sulphuric acid solution, using 800 lb H₂SO₄ per ton of ore; calcined phosphate rock assaying 0.14 pct V₂O₅ and 35.0 pct P₂O₅ was then added to the slurry to raise the pH to about 0.3. The slurry was filtered, the liquor was concentrated by evaporation, and PVA was precipitated in the usual manner. The PVA was then recycled to the roast with the next batch of ore. The results for the last four cycles are summarized in Table 4. The difference

TABLE 4—Treatment of Dry Creek Ore by PVA Ore-roast Process

Cycle No.	Grams Calcined Rock per 1000 Grams Ore	V ₂ O ₅ Extraction ^a in Water Leach, Pct	Total Extraction, ^a Pct	
			V ₂ O ₅	P ₂ O ₅
5	250	80.0	84.8	83.0
6	225	75.0	82.8	89.9
7	240	72.0	87.5	
8	225	94.7	84.5	94.9
Average	235	80.4	84.9	89.3

^a Based on total in ore plus rock added in the cycle.

between the total vanadium extraction of 84.9 pct and the extraction of 80.4 pct in the water leach is due to: (1) loss of about one per cent of the vanadium in the PVA filtrate and (2) variations in the circulating load of PVA.

DIRECT ACID LEACHING OF
PARIS-BLOOMINGTON ORE

Since Paris-Bloomington ore 6-15 does not respond to the PVA ore-roast process, a study was made with the object of extracting the vanadium and phosphate in sulphuric acid solution, precipitating the vanadium as PVA, treating the filtrate to produce phosphate fertilizer, and recovering the vanadium from the PVA by the Anaconda or some other process.

Optimum conditions for extraction were determined to be approximately as follows: ore size, minus 40-mesh; calcining temperature, 800° to 900°C; calcining time,

2½ hr; quantity of acid, 1250 lb per ton calcine (930 lb per ton raw ore); leaching temperature, 70°C; pulp density, 30 pct; leaching time, 4 hr. Under these conditions about 90 pct of the vanadium and phosphate was extracted. When the ore was calcined at minus 4-mesh for 3 hr and then ground to minus 40-mesh before being leached, extractions were the same as when the ore was calcined at minus 40-mesh. Leaching uncalcined ore gave considerably poorer extractions.

Leaching calcined ore with sufficient sulphuric acid to extract about 90 pct of the vanadium and phosphate caused more sulphate than phosphate to be left in PVA filtrates. To improve the grade of the PVA filtrate, leaching tests were made on mixtures of calcined ore 6-15 and calcined phosphate rock 6-14; the calcined ore contained 1.06 pct V₂O₅ and 15.1 pct P₂O₅, and the calcined rock contained 0.14 pct V₂O₅ and 35.0 pct P₂O₅. With a given quantity of acid per ton of mixed calcine, there were no significant differences in extraction of vanadium or phosphate for mixtures ranging from 90 pct calcined ore and 10 pct calcined rock to 50 pct of each; the average extractions were as follows:

H ₂ SO ₄ per Ton Mixed Calcine, Lb	Extraction, Pct	
	V ₂ O ₅	P ₂ O ₅
1125	85	83
1250	89	90
1375	90	91
1500	91	92

Two series of 11-cycle interlocked tests were made, one on calcined ore alone and the other on a mixture of 70 pct calcined ore and 30 pct calcined phosphate rock. In each test 750 grams of calcine was leached for 2 hr at 70°C with 1250 lb H₂SO₄ per ton of calcine at a pulp density of 28 pct solids. The filter cakes were

washed four times countercurrently with water, the wash solutions being advanced from cycle to cycle.

Table 5 gives the average extractions for the last five cycles of each series and the analyses of the pregnant liquors after the eleventh cycle. The addition of phosphate rock greatly improved the ratio of P_2O_5 to SO_3 in the pregnant liquor; the percentage extraction of phosphate was decreased slightly, but approximately 30 pct more P_2O_5 was extracted per unit weight of sulphuric acid used.

liquor is due to retention of the liquor in the filter cake. When the cake is washed with water, the PVA shows a decided tendency to redissolve. For example, when a 50-gram sample of wet unwashed PVA assaying 3.94 pct V_2O_5 , 10.5 P_2O_5 , 1.0 Al_2O_3 , and 41.7 SO_3 was washed by repulping with four 50-ml portions of water, 31.3 pct of the V_2O_5 , 77.2 pct of the P_2O_5 , 96.0 pct of the Al_2O_3 , and 99.6 pct of the SO_3 were extracted, and the final wet cake weighed only 9.3 grams. When dried at $110^\circ C$, the final cake assayed

TABLE 5—*Effect of Presence of Calcined Phosphate Rock in Leaching Calcined Ore*

Ore	Extraction, Pct		Pregnant Liquor, Grams per Liter					Specific Gravity
	V ₂ O ₅	P ₂ O ₅	V ₂ O ₅	P ₂ O ₅	SO ₃	Fe ₂ O ₃	Al ₂ O ₃	
Ore.....	87.2	94.2	6.2	105	121.7	14.1	21.2	1.22
Ore plus phosphate rock.....	88.5	89.5	6.1	179	79.6	4.2	23.8	1.26

PRECIPITATION OF PVA

To precipitate the PVA, the sulphuric acid leach liquor was concentrated by evaporation and oxidized with sodium chlorate. The completeness of precipitation depends largely on the concentration of the liquor, as shown by the data in Table 6. In general, less than 2 pct of the

TABLE 6—*Precipitation of Phosphovanadic Acid*

Specific Gravity of Liquor	Analysis of Wet Unwashed PVA, Pct		Percentage of Total in Unwashed PVA	
	V_2O_5	P_2O_5	V_2O_5	P_2O_5
1.41	20.0	52.5	42.4	5.9
1.53	8.0	22.2	91.2	13.4
1.60	3.3	19.6	99.0	36.4

vanadium was lost in the PVA filtrate when various leach liquors were evaporated to a specific gravity of 1.60 to 1.65. At higher specific gravities the liquors became too viscous to filter.

The decrease in the grade of the PVA with increasing specific gravity of the

39.8 pct V_2O_5 , 38.0 P_2O_5 , 0.7 Al_2O_3 , and 0.3 SO_3 . With a single 50-ml wash, the original wet cake lost 73 pct of its weight and 22.5 pct of the vanadium was extracted; whereas, with a single 25-ml wash, the cake lost 60 pct of its weight and 9.0 pct of the V_2O_5 , 50 pct of the P_2O_5 , and 71 pct of the SO_3 were extracted. The vanadium extracted was actually redissolved from the PVA, since the quantity of vanadium in the liquor retained in the unwashed cake was negligible. Another different sample of PVA assaying 3.5 pct V_2O_5 lost 50 pct of its weight when washed with half its weight of water, and only 3.0 pct of the vanadium was redissolved. Preliminary tests have indicated that much less vanadium is redissolved when PVA is washed with acid-leach liquor than when it is washed with water.

During the evaporation of acid-leach liquors from tests on the composite ore (Table 1) by the PVA ore-roast process a very gelatinous precipitate often appeared when the liquor reached a boiling point

of about 100°C. A typical analysis of the precipitate (dried at 110°C) is: V_2O_5 , 1.1 pct; P_2O_5 , 55.1; Fe, 3.5; Al_2O_3 , 16.9, SO_3 , 10.8; SiO_2 , 0.1; loss on ignition, 10.9. The precipitate tended to redissolve when the evaporation was continued to a boiling point of approximately 112°C, at which the specific gravity of the liquor was 1.6. Such precipitates were not encountered in concentrating acid-leach liquors from any of the other ore samples.

RECOVERY OF VANADIUM FROM PVA *Anaconda Method*

The Anaconda method for recovering vanadium from PVA consists essentially of dissolving the PVA in sodium carbonate to form sodium phosphate and sodium vanadate, precipitating the phosphate as dicalcium phosphate with careful pH control, and finally precipitating the vanadium from the solution as red cake. The calcium precipitate is recycled to the leach.

Tests on this method were made mostly on incompletely washed PVA assaying (undried) 11.4 pct V_2O_5 , 13.9 P_2O_5 , 5.4 SO_3 , 1.0 Fe_2O_3 , and 1.5 Al_2O_3 . Milk of lime and calcium chloride, respectively, were used to precipitate the phosphate.

In the tests with milk of lime the PVA was added slowly to a hot solution containing 1.1 to 1.5 grams of Na_2CO_3 per gram of V_2O_5 charged until the pH was about 6. Then milk of lime was added alternately with portions of the remaining PVA, care being taken to prevent the pH from rising above 8. After the slurry had been agitated for 1 hr milk of lime and sulphuric acid were added alternately, maintaining the pH between 7.5 and 9 until the ratio of CaO to P_2O_5 was approximately 1.3. The slurry was then agitated for 2 hr and filtered. The filtrate contained 75 to 85 pct of the vanadium in the PVA and was virtually free of phosphate. Reagent consumption

per gram of V_2O_5 in the PVA was approximately 1.4 grams of Na_2CO_3 , 3.9 grams of CaO, and 1.1 grams of H_2SO_4 .

In the tests with calcium chloride all the PVA was added to the hot sodium carbonate solution and sufficient powdered Na_2CO_3 was added to raise the pH to 8. The mixture was agitated for an hour. The proper amount of calcium chloride was added as a saturated solution, the pH was brought back to 8 with Na_2CO_3 , and the slurry was finally agitated for 2 hr and filtered. Approximately 2.5 grams of Na_2CO_3 and 7.1 grams of $CaCl_2$ were used per gram of V_2O_5 in the PVA. As before, the filtrate contained 75 to 85 pct of the vanadium, which was readily precipitated as high-grade red cake.

Roast Method

An alternative method for recovering the vanadium from PVA, developed in this investigation, is to roast the PVA with reagents to form insoluble phosphates and then leach the product with water. Although the optimum conditions for this method have not yet been determined, very encouraging results have been obtained. After roasting washed or unwashed PVA for 1 hr at 850° with CaO, $CaCO_3$, MgO, $MgCO_3$, or $MgSO_4$, it has been possible to extract 75 to 90 pct of the vanadium and only a very small part of the phosphorus in a solution from which high-grade red cake could be precipitated by acid hydrolysis. For example, a sample of wet unwashed PVA assaying 4.6 pct V_2O_5 , 13.9 P_2O_5 , 1.8 Al_2O_3 , and 34.6 SO_3 was roasted with one third its weight of $MgSO_4 \cdot 7H_2O$ and leached with water; 83.2 pct of the vanadium and only 0.01 pct of the phosphate were extracted.

PRECIPITATION OF RED CAKE

In all the processes described the vanadium is finally obtained in a solution relatively free of impurities, from which

it is recovered as red cake by acid hydrolysis. To precipitate the red cake, sulphuric acid was added to maintain the pH at 1.2 to 3 and the solution was heated at 85° to 95°C for 4 hr and gently agitated. Under these conditions 97 to 99.8 pct of the vanadium ordinarily was precipitated if the original V_2O_5 concentration of the solution was above 15 grams per liter, the precipitation tending to be more rapid and complete the higher the concentration. Precipitation seldom occurred at initial concentrations below about 10 grams per liter, even with seeding

of the solution was not determined, but red cake assaying only 0.024 pct phosphorus was obtained from a solution containing 18.6 grams of V_2O_5 and 2.2 grams of P_2O_5 per liter. If the solution contains calcium, calcium sulphate will precipitate out when the sulphuric acid is added, and the red cake will be high in sulphur. The calcium may be removed from the solution, however, by the addition of sodium carbonate. Moreover, a large part of the sulphur is eliminated when the red cake is fused to black cake; for example, fusion of a red cake con-

TABLE 7—*Typical Analyses of PVA Filtrates*

Sample	Source	Analysis, Grams per Liter					Specific Gravity
		V_2O_5	P_2O_5	SO_3	Fe_2O_3	Al_2O_3	
A	Dry Creek 1-11 and phosphate rock	1.1	385	253	14.5	69.5	1.58
B	Paris 6-15	1.06	344	355	13.9	67.8	1.62
C	Paris 6-15 and phosphate rock	0.61	496	240	12.9	67.3	1.63

and prolonged agitation. At a pH of about 1.2, the solutions were buffered and the pH remained constant during the precipitation, but at higher pH it was necessary to add acid at frequent intervals to keep the pH constant. Precipitation was usually more rapid and complete at the higher pH (around 3), however, and the total quantity of acid required was less, of course.

The physical nature of the precipitate varied widely, often when the conditions of precipitation were presumably the same. The color of the red cake usually was bright crimson or scarlet but sometimes graded to a dull reddish brown. Although the precipitate was usually very fine grained, it filtered rapidly and could be washed readily. Gentle agitation and uniform heating in a water bath tended to give a uniform product with good physical properties.

No difficulty was experienced in producing red cake of adequate grade. The maximum permissible phosphate content

taining 1.9 pct sulphur yielded black cake containing only 0.17 pct.

In general, the analyses of red cake produced in all the processes studied have been as follows: V_2O_5 , 80 to 90 pct; P, less than 0.01 to 0.03 pct; S, less than 0.01 to 0.03 pct; Na_2O , 1.3 to 10.5 pct; MoO_3 , 0.2 to 3.1 pct; loss on ignition, 5 to 15 pct. The assay of the black cake produced by fusion of the red cake has usually been 90 to 95 pct V_2O_5 and can be calculated accurately from the loss on ignition. Molybdenum follows the vanadium, the ratio of MoO_3 to V_2O_5 in the product being approximately the same as that in the ore.

PHOSPHATE FERTILIZER FROM PVA FILTRATE

Analyses of PVA filtrates obtained in the tests on Dry Creek ore 1-11 (Table 4) and on Paris ore 6-15 (Table 5) are given in Table 7.

Table 8 gives the analyses of the products obtained by treating 100-gram

samples of PVA filtrates B and C with 65 grams of calcined phosphate rock assaying 35.0 pct P_2O_5 . The mixtures were aged for 7 days at room temperature and dried at 110°C. The products were dry and nonhygroscopic and could be ground readily. Data on the quantities

TABLE 8—Neutralization of PVA Filtrates with Calcined Phosphate Rock

Filtrate	Analysis, Pct					
	Total P_2O_5	Ci- trate- insol. P_2O_5	SO_2	Fe_2O_3	Al_2O_3	CaO
B	34.4	5.6	18.9	1.1	4.3	24.6
C	39.7	7.1	12.2	1.1	4.2	

Data	B. Leach- ing Ore 6-15 Alone	C. Leach- ing Mix- ture of Ore 6-15 and Phos- phate Rock
	Pounds	Pounds
Calcined ore leached.....	3200	2240
Calcined rock leached.....		960
Calcined rock for neutrali- zation.....	1400	1280
Citrate-sol. P_2O_5 in fertilizer product.....	790	860
V_2O_5 extracted.....	29.6	22.2

of ore and rock treated and on the yields of vanadium and citrate-soluble phosphate per ton of H_2SO_4 used in leaching are

TABLE 9—Neutralization of PVA Filtrates with Ammonia

Filtrate	Analysis, Pct					
	Total P_2O_5	Ci- trate- insol. P_2O_5	NH_3	SO_2	Fe_2O_3	Al_2O_3
B	26.0	0.5	12.9	25.5	1.1	5.3
C	37.3	0.5	13.3	17.5	0.9	5.0

included in Table 8. The yield of available (citrate-soluble) P_2O_5 (790 and 860 lb per ton H_2SO_4 , respectively) approaches

that for the commercial production of ordinary superphosphate, said by Wagga-man and Easterwood⁹ to require 3.44 tons of 50°Be acid to produce one ton of available P_2O_5 , which is equivalent to a yield of 935 lb per ton of H_2SO_4 .

Tests were also made in which samples of the PVA filtrates were neutralized with ammonia and dried at 110°C. The analyses of the products, which had very good physical properties, are given in Table 9.

SUMMARY

An investigation has been made in the Salt Lake City laboratory of the Bureau of Mines on the treatment of the vanadiferous shales of southwestern Wyoming and southeastern Idaho, which constitute the largest known domestic reserves of vanadium. The results of the investigation may be summarized as follows:

The vanadiferous shales of the Sublette Ridge and Dry Creek areas of south-western Wyoming contain about 1 pct V_2O_5 and 2 or 3 pct P_2O_5 . Approximately 60 to 65 pct of the vanadium can be recovered by the standard roast-leach process, which consists of roasting the ore with salt and pyrite, leaching with water, and precipitating the vanadium as "red cake," a product containing 80 to 90 pct V_2O_5 , by acid hydrolysis of the water extract.

More than 90 pct of the vanadium in the Sublette Ridge ore can be recovered by a process in which the ore is baked with strong sulphuric acid solution and leached with water. A product containing about 40 pct V_2O_5 is precipitated from the water extract and redissolved, the resultant solution is purified, and the vanadium is precipitated as red cake. This process probably is applicable also to Dry Creek ore.

The ores of the Paris-Bloomington area of southeastern Idaho, which contain about 1 pct V_2O_5 and 10 pct P_2O_5 ,

differ considerably in behavior toward the simple roast-leach process. Two samples gave recoveries of 55 to 70 pct of the vanadium, but a third, which had a high calcium carbonate content, proved completely unamenable.

The relatively high phosphate content of the Paris-Bloomington ores makes the recovery of phosphate as well as vanadium worthy of consideration. From ore samples that give substantial extractions of vanadium by the roast-leach process, 80 to 90 pct of both the vanadium and phosphate can be recovered by the following procedure: The ore is roasted with salt and leached with water, the residue is leached with sulphuric acid solution, the acid leach liquor is concentrated by evaporation and oxidized to precipitate the vanadium as phosphovanadic acid (PVA), and the PVA is recycled to the salt roast. All the vanadium in the PVA as well as part of the vanadium in the ore is extracted in the water leach and can be recovered as red cake. The PVA filtrate can be converted to phosphate fertilizer.

The sample of Paris-Bloomington ore that was not amenable to treatment by the simple roast-leach process was also not amenable to the PVA ore-roast process outlined above. However, about 90 pct of the vanadium and phosphate can be recovered by the Anaconda process, in which the calcined ore is leached with sulphuric acid, PVA is precipitated from the leach liquor, and the vanadium is recovered from the PVA. The vanadium can be recovered from the PVA by two methods: (1) the Anaconda method, in which the washed PVA is dissolved in sodium carbonate solution, the phosphate is precipitated by the addition of lime or calcium chloride with careful pH control, and the vanadium is precipitated as red cake from the resulting solution, and (2) a new method in which the washed or unwashed PVA is roasted with CaO ,

CaCO_3 , MgO , MgCO_3 , or MgSO_4 , the roasted product is leached with water, and red cake is precipitated from the solution.

The PVA ore-roast process can be applied to Dry Creek ore (and presumably to Sublette Ridge ore) by adding phosphate rock to the water-leach residue, leaching with sulphuric acid, precipitating PVA, and recycling the PVA to the salt roast; 80 to 90 pct of the total vanadium and phosphate in the ore and phosphate rock can be recovered in this manner.

Fusion of the red cake produced by all the processes discussed has yielded commercial-grade "black cake" containing 90 to 95 pct V_2O_5 and less than 0.05 pct phosphorus or sulphur.

Fertilizer products of good physical properties can be prepared by treating the PVA filtrates with phosphate rock or with ammonia. Products containing 29 to 33 pct available P_2O_5 were obtained by treatment with phosphate rock, and products containing 25 to 37 pct available P_2O_5 and about 13 pct NH_3 were obtained by treatment with ammonia.

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The Unit Processes of Chemical Metallurgy

By R. SCHUHMAN, JR.,* MEMBER AIME

(New York Meeting, February 1948)

THE expression "unit process" comes up with increasing frequency in discussions among metallurgists and mineral engineers, especially among those concerned with training the next generation. The unit process approach characterizes a significant advance along the road from metallurgy as an empirical art to metallurgy as a branch of engineering. The purposes of this paper are to define and list the unit processes in specific terms, to indicate the scientific and engineering principles basic to all the unit processes, and finally to show how these ideas have been applied to a reorganization of instruction in chemical metallurgy.

UNIT OPERATIONS AND UNIT PROCESSES

Metals are extracted from ores and other raw materials by stepwise procedures. In general, each metallic element is extracted by a different procedure. For many of the metals there is a choice of several flowsheets. However, the procedures all have steps in common. In fact, the many different flowsheets are all made up of a relatively small number of steps which are combined in different groups and sequences. For example, crushing, screening, roasting, sintering, melting, and gaseous reduction are steps which each appear in the flowsheets for extracting the majority of the metals.

The individual steps or flowsheet units can be designated as *unit operations* or *unit processes*. These terms are well established

in the field of chemical engineering, as the American Institute of Chemical Engineers' definition of chemical engineering shows:

"Chemical engineering is that branch of engineering concerned with the development and application of manufacturing processes in which chemical or certain physical changes of materials are involved. These processes may usually be resolved into a coordinated series of unit physical operations and unit chemical processes. The work of the chemical engineer is concerned primarily with the design, construction, and operation of equipment and plants in which these unit operations and processes are applied. Chemistry, physics, and mathematics are the underlying sciences of chemical engineering, and economics its guide in practice."^{1a}

In this definition, the distinction between unit operations and unit processes is that the *unit operations* are *physical* while the *unit processes* are *chemical*. Table 1 gives a list of the principal unit operations and unit processes of chemical engineering, taken from Shreve.^{1b}

Table 2 lists the principal unit operations and unit processes used for metal extraction. The division between unit operations and unit processes is similar to the chemical engineers' distinction and also corresponds approximately to the division of labor between mineral dressing and chemical metallurgy which has been customary in the past. Furthermore, it will be noted that in the proposed classification the *unit processes primarily involve chemical reactions and/or changes in state of aggregation; the unit operations primarily do not involve either bulk*

Manuscript received at the office of the Institute November 29, 1947; revision received February 27, 1948. Issued as TP 2363 in METALS TECHNOLOGY, June 1948.

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^{1a} References are at the end of the paper.

reactions or changes in state. Other bases of classifying as between unit operations and unit processes might be preferred, or precise definitions might be avoided. However, it is intended here to include in the field of chemical metallurgy only those unit actions in which chemical reactions and changes in state are performed, and henceforth in this paper these will be called unit processes.

Mineral dressing literature and education have long been organized on a unit operations basis, though not originally so labelled. Thus the chapter headings in Professor Richards' original "Ore Dressing" of 1903 as well as in Professor Gaudin's, "Principles of Mineral Dressing" of 1939 are mainly unit operation names. The change of ore dressing to mineral dressing exemplifies a conscious recognition and acceptance of the unit operations idea.

TABLE 1—Principal Unit Operations and Unit Processes of Chemical Engineering (from Shreve, "The Chemical Process Industries")

UNIT OPERATIONS	UNIT PROCESSES
Fluid flow	Combustion
Heat transfer	Oxidation
Evaporation	Neutralization
Humidification and dehumidification	Silicate formation
Gas absorption	Causticization
Solvent extraction	Electrolysis
Adsorption	Double decomposition
Distillation and sublimation	Calcination
Drying	Nitration
Mixing	Esterification
Classification	Reduction
Sedimentation and decantation	Ammonolysis
Filtration	Halogenation
Screening	Sulfonation
Crystallization	Hydrolysis
Centrifugation	Hydrogenation
Disintegration	Alkylation
Materials handling	Friedel-Crafts
	Condensation
	Polymerization
	Diazotization and coupling
	Fermentation
	Pyrolysis
	Aromatization
	Isomerization

In contrast, in the field of chemical metallurgy greater emphasis has been placed on the materials being treated. Thus, instead of a unit process organization there has been a division into ferrous and nonferrous metallurgy, the nonferrous covering copper, lead, zinc, precious metals, light metals, minor metals, and the like, as separate

TABLE 2—Principal Unit Operations and Unit Processes for Extracting Metals

UNIT OPERATIONS	UNIT PROCESSES
Comminution	Gas-solid processes (including roasting, calcining, gaseous reduction and drying)
Screening	Sintering and pyroagglomeration
Classification	Melting and liquation
Heavy-fluid separation	Reduction of metal oxides
Jigging	Simple smelting
Flowing film concentration and tabling	Blast furnace smelting
Flotation and agglomeration	Converting
Magnetic separation	Retorting
Electrostatic separation	Refining of liquid metals
Separation of solids from fluids	Distillation and sublimation
Agitation and mixing	Casting and solidification
Materials handling	Hydrometallurgical processes
	Electrolytic processes

categories. College courses organized along these lines generally have been accompanied by courses in General Metallurgy, Principles of Metallurgy, and Metallurgical Calculations which follow unit process ideas to a considerable degree.

BASIS OF CLASSIFYING THE UNIT PROCESSES

A primary purpose of unit process classification is to group like with like. In a given unit process we are dealing with a certain kind of system. The principles governing the behavior and operation of a certain kind of system are generally the same regardless of the chemical composition, temperature, pressure, size, and so forth. The clearest differentiation among the unit processes listed in Table 2 is on the basis of the kinds of phases involved in the system. For example, melting is a solid-liquid transformation; simple smelting involves production of two or more liquid phases; refining of molten metals involves addition of reagents (usually solid or gaseous) to impure liquid metal with the removal of the impurity to another phase (gas, liquid, or solid); hydrometallurgical processes involve reactions of aqueous solutions and solids. Reduction of metal oxides is carried out in systems of various combinations of phases and overlaps the other unit processes, but is listed separately because of the important group of principles concerned.

One useful and significant result of classifying unit processes according to the important phases handled is that processes carried out in similar apparatus are grouped together. For example, any simple smelting operation can be conducted in a reverberatory furnace, an arc furnace, or a crucible. A gas-solid reaction, whether calcining, desulphurization roasting, or gaseous reduction, can be carried out in a multiple-hearth furnace, a rotary kiln, a muffle, a fluidized-solid system, a flash system, or a combustion boat in a tube furnace.

It is interesting to note the relatively small number of unit processes in extractive metallurgy. With these thirteen unit processes, and a similar number of unit operations, all the scores of flowsheets of metal extraction are readily synthesized.

SCIENTIFIC AND ENGINEERING FUNDAMENTALS

Since the unit processes deal with chemical reactions and changes in state, it follows that their basic science is chemistry. The last ten years have brought wide recognition among metallurgists of the value of chemical thermodynamics as a working tool. As the thermodynamics becomes taken for granted, so it becomes increasingly evident that it does not give the whole story; and therefore metallurgists are starting to delve into reaction kinetics, surface chemistry, and other branches of chemical science.

Accepting the standard engineering college training in mathematics, physics, and chemistry plus advanced study of physical chemistry as the scientific foundation of the unit processes, there remains certain engineering training which should precede or accompany the study of unit processes. It is in respect to this engineering training that metallurgy graduates have suffered in competition with chemical engineers. Specifically, there are in common among all the unit processes a number of principles

and types of problems for which a quantitative engineering approach is essential, whether or not a thorough scientific understanding can be had. Table 3 lists these engineering subjects.

TABLE 3—*Engineering Bases of the Metallurgical Unit Processes*

Stoichiometry
Thermochemistry and thermophysics; heat balances
Fuels and combustion
Pyrometry
Flow of heat
Flow of fluids
Phases and phase equilibria in metallurgical systems
Retractories and furnaces
Mass action
Rates of reaction
Instrumentation and control

The list in Table 3 represents to a considerable extent the subject matter of "Metallurgical Calculations." However, it is this author's impression that courses in Metallurgical Calculations have outgrown their usefulness. This material should not be considered as merely calculation or computation but as a broad engineering study.

INTEGRATED PROCESSES

So far we have looked at unit processes and then looked behind them at the basic science and engineering. Now we must look beyond the unit processes and consider their integration with each other and with metallurgical arts, economics, and common sense in the form of flowsheets and plant operations.

Most students learn more easily if they can get occasional broad glimpses of ultimate application; also they digest more or less abstract principles much better when the principles are leavened with descriptive material and practical examples. To these ends, it is desirable to commence the study of chemical metallurgy with a brief survey of typical flowsheets presented with few details and then, during the intensive study of engineering principles and unit processes, to bring in practical examples which tie things together. In this connection also plant visits are very helpful.

After the student gets a good foundation

in the sciences, the unit processes, the unit operations, the engineering, and economics, he must integrate them and learn to bring them all to focus on a practical situation through the lens of good judgment. This aspect of metallurgical education cannot be broken down and tabulated. However, it is clear that an important function of the college training is to start this integration in the right direction.

Near the end of the undergraduate work a course devoted to the study of flowsheets, integrated plants, and operating problems should afford a favorable opportunity for the teacher to assist the student in bringing to focus the various elements he has been studying separately. Such a course might well be conducted on a "case" basis. In this author's opinion, neither this course nor any other undergraduate college course should attempt as a major objective to impart extensive knowledge of metallurgical arts.

LABORATORY

The laboratory must play a vital role in a unit process program. This role probably can be served best in undergraduate work by experiments with small scale equipment which an individual student or a group of two or three can operate successfully in a reasonable time. From experience of the past, it is clear that small scale and portability are essential if a flexible up-to-date program is to be maintained at reasonable cost. Quantitative experiments designed to illustrate one or two principles at a time are more important than qualitative experiments which illustrate the art. For quantitative experiments we can in many cases adapt apparatus which has been developed in the past for research purposes. Most of the apparatus will have to be designed and built; little can be bought outright.

In the early stages of developing such a program at Mass. Inst. of Tech., the attempt is being made to achieve a balance among experiments along these lines: (1)

high temperature chemistry, equilibria, and reaction rates; (2) engineering studies on subjects listed in Table 3; and (3) specific unit processes (see Table 2).*

APPLICATION OF UNIT PROCESS APPROACH TO THE CURRICULUM

On the basis of the reasoning outlined in foregoing paragraphs, there has been set up at Mass. Inst. of Tech. a sequence of three unit process courses, called Metallurgical Engineering I, II, and III. Information on these courses is summarized in Table 4. As the catalogue descriptions indicate, the analysis and solving of problems are emphasized throughout the sequence. With the institution of these courses, the traditional courses in Nonferrous Metallurgy, Metallurgy of Iron and Steel, Metallurgical Calculations, and General Metallurgy are being dropped from the curriculum.

Closely related to the unit process subjects, of course, are the unit operation subjects in Mineral Engineering. Both have in common the "unit" viewpoint and both have the common objective of separating substances from each other. Also, integrated flowsheets are as often as not composed of both unit operations and unit processes.

In addition to physical chemistry taken in the Chemistry Department in the junior year, all students take Metallurgical Thermodynamics in the senior year. The latter course is taught in the Metallurgy Department so that a close relationship between the science and engineering of chemical metallurgy is fostered in the student's mind.

In addition to the three basic courses indicated in Table 4, the student may elect more advanced or specialized work in chemical metallurgy. The elective program

* These are in addition to a course in Heat Measurements taken by the students in the Mechanical Engineering Department which among other things affords a good coverage of pyrometry.

is not fully developed, but includes at present Principles of Steelmaking, Advanced Nonferrous Metallurgy, Applied Electrochemistry, and Special Problems.

graduate study. Also it affords an opportunity for winding up the springs of imagination, originality, and resourcefulness which can lie dormant through years

TABLE 4—Unit Process Courses at Mass. Inst. of Tech.

Name of Course	Hours per Week			Content	Catalogue Description
	Lecture and Recitation	Laboratory	Nominal Preparation		
Met. Engr. I	4	0	4	Engineering common to all unit processes, outlined in Table 3	"Principles underlying the unit processes by which metals are extracted from ores and other raw materials. Emphasis on those principles common to all metallurgical processes involving chemical reactions or changes in state. Metallurgical stoichiometry, thermochemistry and thermophysics, heat balances, fuels and combustion, fluid flow, heat transfer, refractories, physical and chemical attributes of the solid and liquid phases in metallurgical systems, mass action, reaction rates. Quantitative application of these principles to metallurgical engineering problems."
Met. Engr. II	3	4	6	Unit processes, outlined in Table 2	"The unit processes used in extracting metals from ores and other raw materials. Gas-solid processes (roasting, calcining, and drying), sintering, reduction of metal oxides, smelting, converting, distillation, and refining processes studied from the standpoint of the principles introduced in Metallurgical Engineering I. Apparatus, design and operating variables, and engineering calculations for the important unit processes. Hydrometallurgical and electrometallurgical processes considered briefly. Recognition and measurement of the important variables in typical metallurgical processes and small-scale process equipment stressed in laboratory practice."
Met. Engr. III	2	0	4	Flowsheets and integrated processes on case study basis	"Integrated metallurgical engineering processes. Synthesis of the principles, unit operations, and unit processes studied in preceding courses in mineral and metallurgical engineering with emphasis on the development of complete flowsheets for producing metals from ores. Economic and other considerations involved in choice of process. Production metallurgy of iron and steel and of the important nonferrous metals."

Finally, in the last half of his senior year each student carries out a thesis investigation in the laboratory and prepares a finished thesis report, representing a total of at least 180 hr of work (12 credit hr). The thesis project is an introduction to research methods and the research viewpoint, and to high standards of observing, recording, and reporting experimental work. In these respects it should be particularly valuable to students not planning

of formal courses. Obviously care must be taken in choice of senior thesis topics. Repetitions and extensions of older published researches, development of laboratory apparatus, and development of experiments for the undergraduate laboratory offer many possibilities. Current topics in chemical metallurgy include: dissociation pressures of carbonates, gas solubilities in liquid alloys, gas-solid reactions in fluidized-solid systems, pelletizing

iron ore, and vapor pressures of liquid metals and alloys.

This paper has been confined largely to unit processes of chemical metallurgy and the most closely related subjects. Many other questions come up when the designing of a complete and consistent four or five year curriculum is considered. Thus the unit processes of chemical metallurgy may form part of at least three different curricula: (1) metallurgy, (2) mineral engineering, or (3) chemical engineering. The unit process approach is equally sound for all three curricula.

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DISCUSSION

(C. H. Behre, Jr., and R. T. Gallagher presiding)

F. R. MORRAL*—The philosophy of unit operations and unit processes of Chemical Metallurgy presented in this paper has been needed for some time in Metallurgical Engineering Education. It helps simplify the study of our detailed engineering knowledge. I wonder if it would not be desirable to go further and consider as a group unit processes for Processing Metals, whose fundamental principles also apply both to ferrous and non-ferrous metals. A list could be made, similar to that of Table 2, and it may read as follows:

1. Casting (ingots, die casting, to lost wax process).
2. Working (forging, rolling, drawing, etc. to spinning).

* American Cyanamid Co.

3. Heat treating (from softening to hardening¹).
4. Joining (soldering, brazing to welding).
5. Surface treatments.²

Some eight years ago,³ an attempt was made to call attention to the steps necessary to all types of coating processes, from painting to hot dipping and electroplating.

E. A. PERETTI*—Dr. Schuhmann is to be congratulated for giving us this interesting account of the organization at M.I.T. of courses in unit operations and unit processes for metallurgy students.

Many of us have been struggling with this problem for several years. At Columbia in 1940, under the initiative of Dr. E. R. Jette, we started a similar program which was also based on the kinds of phases involved in a given system. One of the greatest obstacles encountered was the lack of information regarding the kinetics of the reactions of metallurgical importance. In too many cases it was found that reaction mechanisms are unknown, and what is worse (this seems to be especially true of the nonferrous field) very few attempts are being made to shed light on this phase of metallurgical processes.

It is my belief that the unit operations and unit processes approach to teaching has the beneficial effect of producing metallurgists who have a better knowledge and keener interest in the fundamentals involved, although they may have a poorer knowledge of the art.

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² F. R. Morral: *Surface Treatments for Metals*. Wire and Wire Products, April 1945, p. 272.

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